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Analytische Methoden mit KOMPLEXON*

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ON THE REACTIVITY OF BENZIDINESULFONIC ACIDS AND THEIR APPLICATIONS IN ANALYSIS

REACTION OF CUPRIC SALTS WITH *O*-BENZIDINEMONOSULFONIC ACID IN PRESENCE OF ALKALI THIOCYANATE

by

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Part of our research work on the reactivity of benzidinedisulfonic acids has already been published^{1,2,3}. We study in the present paper the reaction which takes place when first ammonium thiocyanate and then a solution of the ammonium salt of *o*-benzidinemonosulfonic acid are added to a cupric salt.

Under such conditions we do not observe the red precipitate described in one of the papers mentioned above and given by cupric salts with the same acid when thiocyanates are not present, but another one, blue, and flaky when the copper concentration is sufficiently high. At lower concentrations there is only a blue coloring.

In order to obtain this precipitate or coloring, it is necessary — as in all reactions given by cupric salts with other amines, thiocyanates being present — that the initial concentrations of Cu^{II} should be low enough to avoid the precipitate of cupric thiocyanate; in this case, a slight excess of SCN^- is also necessary, otherwise the red precipitate already described and which appears in solutions that are SCN^- -free might form after the blue precipitate.

This reaction provides a new specific qualitative test for the Cu^{II} with a sensitivity of $1/500,000$ ($10^{-5.7}$).

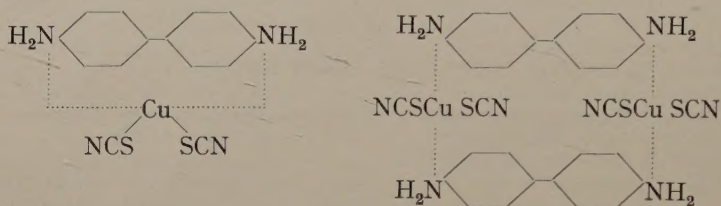
As this reaction is only given by *o*-benzidinemonosulfonic acid among the three benzidinesulfonic acids we have studied, it can also be used to distinguish quickly the *o*-benzidinemonosulfonic acid from *o*-*o'*-disulfonic and *m*-*m'*-disulfonic acids. At the same time this behaviour is another proof of the influence of the $-\text{SO}_3\text{H}$ group on $-\text{NH}_2$ benzidinic groups. When two sulfonic groups are present it can even inhibit the reaction, showing an analogy with other substituents such as $-\text{OCH}_3$ in the reactivity of *o*-dianisidine with regard to the benzidine.

We did not use this reaction for the gravimetric estimation of copper in spite of its high sensitivity, as it is very difficult to obtain a readily filtrable precipitate without any loss of Cu^{II} , this being due to its easy peptization. Peptization is increased by the presence of an excess of reagent, but this excess is essential to ensure a complete precipitation of the copper. It may be possible, however, to use the reaction as a base for a colorimetric method.

Considerations about the possible mechanism of the reaction

This is just one of the problems concerning the formation of blue precipitates by various aromatic amines under the same conditions, for which different interpretations have been proposed.

The precipitate given by benzidine and copper salts, thiocyanates being present, has been studied by SPACU^{4,5} who proposed, as possible formulae of these compounds, the following complex formulae:



We studied the reaction given by *o*-dianisidine under the same conditions⁶ and we indicated this possible formula (Cu-*o*-dian) (SCN)₂.

The reaction of α -naphthylamine under the same conditions was also studied by us⁷ and the formation of meriquinoid compounds by means of oxydation was admitted as possible.

It has not yet been decided whether the mechanism of the reaction involves the formation of complex salts as was originally proposed by SPACU, or whether it might be an oxidation process of the amine leading to the formation of a blue meriquinoid compound, as proposed by TETTAMANZI AND FEIGL in the case of benzidine, and by ourselves in the case of α -naphthylamine. In a similar reaction when potassium mercuric thiocyanate is present, SIERRA is rather inclined to admit the formation of complexes.

There are many arguments for and against both theories. On the one hand there are some non-oxidizable substances that yield blue products, as for instance, the pyridine giving blue precipitates with copper in presence of thiocyanate. But, on the other hand, if the reaction of many aromatic amines with cupric thiocyanate is carried out, it can be observed that blue precipitates are given only by amines that are easily oxidized by oxidizing agents — blue meriquinoid compounds being formed — while the non-oxidizable amines do not give such precipitates. For instance, benzidine, *o*-tolidine, *o*-dianisidine and α -naphthylamine, the reactions of which with the oxidizing agents are known, react well with SCN⁻ and Cu^{II}, but as we have indicated⁷, β -naphthylamine does not. β -Naphthylamine also does not give the usual oxidizing reactions of its α -isomer.

The oxidizing action of cupric thiocyanate could be easily explained in view of its easy transformation into cuprous thiocyanate while sulfocyanogen is set free; this process appears to explain the high sensitivity that this sort of reaction provides if we bear in mind that:

- oxidation leads to the formation of a product with a great coloring intensity.
- the nascent sulfocyanogen is a pseudohalogen of considerable oxidizing power, intermediate between that of iodine and that of bromine.

c) The formation of free sulfocyanogen is favoured by the small solubility product of cuprous thiocyanate ($4 \cdot 10^{-14}$) which is smaller than the solubility product of cuprous iodide ($1.1 \cdot 10^{-10}$). These considerations are in accordance with the following fact which we have checked experimentally: the reaction carried out either with benzidine or *o*-dianisidine with different copper halides (chloride, bromide, iodide and thiocyanate) is given by thiocyanate with maximum intensity.

This mechanism of oxidation has another test in its favour, *viz.* the behaviour of these three benzidine sulfonic acids. *o*-Monosulfonic acid which is the acid that more easily gives general oxidation reactions^{1,2} is at the same time the only one that gives this special reaction with cupric thiocyanate. It seems permissible, in view of this fact, to consider that the reaction occurs in the simple manner of formation of a cuprous salt and a blue meriquinoid compound. This oxidation is probably already linked to the simultaneous formation of coordination complexes.

In addition to these observations there is also the fact that the precipitate does not show a perfectly defined composition but, on the contrary, if sufficient quantities of reagent are used, intermediate compounds are obtained whose percentage of copper is not constant and always greater than the percentage obtained when an excess of reagent is used.

On the other hand, the results given by the analysis of the precipitate do not justify (as shown in the experimental part) a formula of inner complex with two molecules of the reagent for one copper atom; neither do they meet the formulae SPACU suggested, as the difference between the results of the analysis and the theoretical values calculated for these formulae is so great that it could not be explained even by the great tendency of these blue precipitates to absorb the copper salts present.

EXPERIMENTAL PART


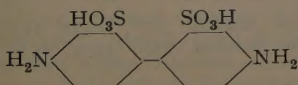
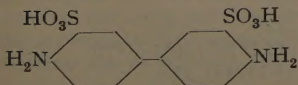
Solutions to be analysed. 1M Copper nitrate, copper chloride and copper sulfate solutions are used.

Reagent solution. (a) 15 g of purified benzidine-*o*-monosulfonic acid are weighed and transferred to a 500 ml capsule; 5 ml of NH_4OH are added drop by drop; the pulp thus formed takes slowly a reddish brown colour. If necessary 2 more ml are added, as well as 400 ml of distilled water. If the pH of the solution is greater than 7, one or two grams of solid reagent are added until the pH is brought down to the desired value. The solution is diluted to 1000 ml and after filtering the filtrate is used as a reagent.

(b) Normal solution of ammonium thiocyanate.

Qualitative behaviour of the three sulfonic acids

The reagent solutions of the *o*-*o'*-benzidinedisulfonic and *m*-*m'*-benzidinedisulfonic acids have been similarly prepared. Their behaviour with Cu^{II} has been studied (5 ml of CuSO_4 (1%) + 2 ml NH_4SCN + 3 ml of the reagent).

Salt of the acid	In the cold	From hot solutions
	Abundant blue precipitate soluble in NO_3H and NH_4OH	It agglomerates and turns greenish
	Nothing	Nothing
	After a few minutes a greenish cloudiness appears	

Method for the identification of Cu^{II} . 2 drops of the solution under examination are deposited on a drop plate; the solution has been previously diluted just enough to avoid the precipitation of the copper with the thiocyanate; 3 drops of normal potassium thiocyanate and one drop of reagent are added. When Cu^{II} is present a blue coloring or a blue precipitate appears.

The precipitate is soluble in dilute mineral acids and in ammonium hydroxide and a further addition of alkalis or acids respectively does not produce its precipitation. It is insoluble in usual organic solvents. When heated it takes a greenish colour and when ignited it gives CuO .

Sensitivity of the reaction. The blue precipitate can be observed with a 1/100,000 concentration. The blue coloring persists and can be clearly seen with concentrations somewhat greater than 1/500,000. Therefore, the limit of the dilution can be considered to be $10^{-5.7}$.

Composition of the precipitate. Many precipitates have been prepared following the method indicated below and using copper chloride as unknown solution.

Preparation of the precipitate in view of its analysis. 100 ml of the solution of copper salt are diluted to 500 ml and heated to about 60-70° C. Immediately after the slow addition of 50 ml of the normal solution of thiocyanate, the reagent solution is added until the precipitation is complete. Care must be taken to keep on stirring to avoid absorption. (If an excess of reagent is not used, intermediate compounds might form which have a greater copper content than the precipitate being studied; that occurs possibly as a consequence of the strong absorption shown by these precipitates and the copper salts.)

The precipitate is filtered through a sintered glass crucible (G-4) washed with water and dried to constant weight at 105° C.

Copper estimation. Carried out by calcination up to CuO (Average: 16.4% Cu).

Sulphur estimation. The process consists of the oxidation according to Liebig's method, using potassium hydroxide and potassium nitrate. The sulfate is weighed as barium sulfate. (Average: 18.4% S).

Nitrogen estimation. Following Kjeldahl's method, modified by Jodlbauer. (Average: 11.1% N).

SUMMARY

In the present work a new method for the detection of copper(II) is described. It is based on the reaction of this ion with the alkali salts of *o*-benzidine monosulfonic acid, alkali thiocyanate being present. The sensitivity of this test is 1/500,000 ($10^{-5.7}$); it is specific for the Cu^{+2} ion and can also be used to distinguish quickly the above-mentioned acid from the benzidine *o-o'*-disulfonic and benzidine *m-m'*-disulfonic acids. It is believed that the mechanism of the reaction can be explained by an oxidation process.

RÉSUMÉ

Le présent exposé traite d'une nouvelle méthode pour la recherche du cuivre(II), basée sur sa réaction avec les sels alcalins de l'acide *o*-benzidine monosulfonique, en présence de thiocyanates alcalins. La sensibilité de cette réaction est de 1/500,000 ($10^{-5.7}$); l'essai est spécifique de l'ion Cu^{+2} et peut être aussi appliqué pour différencier rapidement l'acide précité des acides benzidine *o-o'*-disulfonique et *m-m'*-benzidine disulfonique. Il semble que le mécanisme de la réaction peut s'expliquer par un processus d'oxydation.

ZUSAMMENFASSUNG

In der vorliegenden Arbeit wird eine neue Methode für den Nachweis von Kupfer(II) entwickelt. Sie geht von der Reaktion dieses Ions mit den Alkalisalzen der *o*-Benzidin-monosulfosäure in Gegenwart von Alkalithiocyanaten aus. Die Empfindlichkeit von dieser Prüfungsmethode beträgt 1/500,000 ($10^{-5.7}$). Die Reaktion ist spezifisch für das Cu^{+2} -Ion und erlaubt die sofortige Unterscheidung der obengenannten Säure von Benzidin-*o-o'*-disulfosäure und *m-m'*-disulfosäure. Es scheint dass der Mechanismus der Reaktion mit Hilfe eines Oxydationsprozesses erklärt werden kann.

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DIETHYLENETETRA-AMMONIUM SULPHATOCERATE AS VOLUMETRIC REAGENT

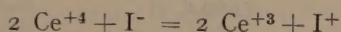
II. IODINE MONOCHLORIDE METHOD. INDIRECT DETERMINATIONS*

by

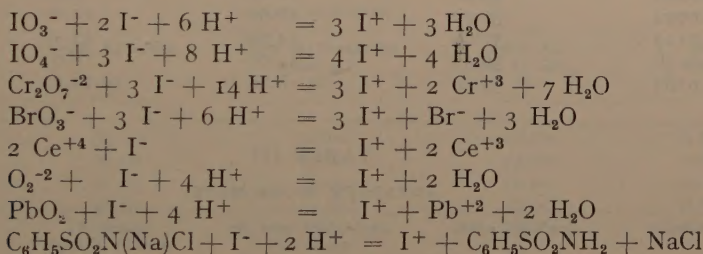
BALWANT SINGH AND SURJIT SINGH

Panjab University College, Hoshiarpur (India)

In acid medium diethylenetetra-ammonium sulphatocerate, $[\text{Ce}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2)_2](\text{SO}_4)_2 \cdot 2\text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, reacts with potassium iodide:



In presence of hydrochloric acid, potassium iodide reacts with potassium iodate, potassium metaperiodate, potassium dichromate, potassium bromate, ceric sulphate, hydrogen peroxide, lead dioxide and chloramine-B according to the following equations:



The reactions have been utilized for the quantitative determination of the substances.

EXPERIMENTAL

A known amount of each substance was transferred to a conical flask, and 5 ml of chloroform, a known excess of potassium iodide solution and enough hydrochloric acid to keep its normality between 4N to 6N were added. The excess of potassium iodide was titrated with diethylenetetra-ammonium sulphatocerate (DTS) solution. The reagent was added from a burette until the solution which was coloured with iodine became pale yellow and the chloroform layer acquired a purple colour. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of the sulphatocerate solution was continued, shaking vigorously after each addition, until the chloroform layer was faintly violet. The sulphatocerate solution was then added dropwise, with shaking after the addition of each drop, till the chloroform layer became pale yellow. The end-point was very sharp.

Several titrations were performed in each case. From the volume of diethylenetetra-ammonium sulphatocerate (DTS) used, corresponding to the end-point in each titration, the amount of each substance was calculated. The results are recorded in Tables I-VIII. From these results it is con-

* PART I was published in *Anal. Chim. Acta*, 14 (1956) 109.

cluded that diethylenetetra-ammonium sulphatocerate (DTS) can be used as a volumetric reagent to determine indirectly potassium iodate, potassium metaperiodate, potassium dichromate, potassium bromate, ceric sulphate, hydrogen peroxide, lead dioxide and chloramine-B by the iodine monochloride method.

All chemicals, except ceric sulphate and chloramine-B, used in this investigation were of guaranteed purity. Ceric sulphate was standardized with ferrous ethylenediamine sulphate. Chloramine-B was freshly prepared and standardized by an iodometric method.

TABLE I
POTASSIUM IODATE

KIO_3 taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by KIO_3 ml	KIO_3 found g
0.0092	30.00	21.40	8.60	0.0092
0.0123	30.00	18.50	11.50	0.0123
0.0153	30.00	15.70	14.30	0.0153
0.0189	30.00	12.30	17.70	0.0189
0.0215	30.00	9.90	20.10	0.0215

TABLE II
POTASSIUM METAPERIODATE

KIO_4 taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by KIO_4 ml	KIO_4 found g
0.0069	30.00	21.00	9.00	0.0069
0.0092	30.00	18.00	12.00	0.0092
0.0119	30.00	14.50	15.50	0.0119
0.0138	30.00	12.00	18.00	0.0138
0.0163	30.00	8.80	21.20	0.0163

TABLE III
POTASSIUM DICHROMATE

$K_2Cr_2O_7$ taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by $K_2Cr_2O_7$ ml	$K_2Cr_2O_7$ found g
0.0083	30.00	21.50	8.50	0.0083
0.0108	30.00	19.00	11.00	0.0108
0.0140	30.00	15.70	14.30	0.0140
0.0169	30.00	12.80	17.20	0.0169
0.0210	30.00	8.60	21.40	0.0210

TABLE IV
POTASSIUM BROMATE

$KBrO_3$ g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by $KBrO_3$ ml	$KBrO_3$ found g
0.0056	30.00	20.00	10.00	0.0056
0.0072	30.00	17.00	13.00	0.0072
0.0091	30.00	13.60	16.40	0.0091
0.0114	30.00	9.55	20.45	0.0114
0.0128	30.00	7.05	22.95	0.0125

TABLE V
CERIC SULPHATE

$Ce(SO_4)_2$ taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by $Ce(SO_4)_2$ ml	$Ce(SO_4)_2$ found g
0.0618	30.00	20.70	9.30	0.0618
0.0811	30.00	17.80	12.20	0.0811
0.0997	30.00	15.00	15.00	0.0997
0.1196	30.00	12.00	18.00	0.1196
0.1475	30.00	7.90	22.10	0.1469

TABLE VI
HYDROGEN PEROXIDE

H_2O_2 taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by H_2O_2 ml	H_2O_2 found g
0.0044	30.00	17.00	13.00	0.0044
0.0053	30.00	14.50	15.50	0.0053
0.0062	30.00	11.80	18.20	0.0062
0.0073	30.00	8.65	21.35	0.0073
0.0089	30.00	3.95	26.05	0.0089

TABLE VII
LEAD DIOXIDE

PbO_2 taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by PbO_2 ml	PbO_2 found g
0.0239	30.00	20.00	10.00	0.0239
0.0311	30.00	17.00	13.00	0.0311
0.0383	30.00	14.00	16.00	0.0383
0.0454	30.00	11.00	19.00	0.0454
0.0502	30.00	9.00	21.00	0.0502

TABLE VIII
CHLORAMINE-B

$C_6H_5SO_2N(Na)Cl_3H_2O$ taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by $C_6H_5SO_2N(Na)Cl_3H_2O$ ml	$C_6H_5SO_2N(Na)Cl_3H_2O$ found g
0.0187	30.00	23.00	7.00	0.0187
0.0294	30.00	19.05	10.95	0.0293
0.0385	30.00	15.65	14.35	0.0384
0.0463	30.00	12.75	17.25	0.0461
0.0586	30.00	8.10	21.90	0.0586

SUMMARY

In presence of 4N to 6N hydrochloric acid, diethylenetetra-ammonium sulphatocerate was used as a volumetric reagent to determine indirectly potassium iodate, potassium metaperiodate, potassium dichromate, potassium bromate, ceric sulphate, hydrogen peroxide, lead dioxide and chloramine-B by the iodine monochloride method. An excess of potassium iodide added to each

of the substances in the acid medium was titrated back with a standard solution of diethylene-tetra-ammonium sulphatocerate. Chloroform was used as an indicator. It was coloured violet owing to the liberation of iodine during the titration and became very pale yellow at the end-point because of the formation of iodine monochloride.

RÉSUMÉ

Le sulfate de di(éthylènediamino)-cérium (IV), en présence d'acide chlorhydrique 4 à 6N a été utilisé comme réactif pour le dosage volumétrique indirect de l'iodate, du métaperiodate, du dichromate et du bromate de potassium, du sulfate cérique, du peroxyde d'hydrogène, du dioxyde de plomb et de la chloramine B, par la méthode au monochlorure d'iode. L'excès d'iodure de potassium, ajouté à chacune de ces substances, en milieu acide, est titré par une solution étalon de sulfate de di(éthylènediamino)-cérium(IV). Le chloroforme est utilisé comme indicateur; il se colore en violet par l'iode libéré pendant le titrage et devient jaune très pâle au point final par formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Das Cer(IV)di(äthylendiamin)sulfat, wurde in Gegenwart von 4-6N Salzsäure als Reagenz für die indirekte volumetrische Bestimmung von Jodat, Metaperjodat, Bichromat, Kaliumbromat, Cersulfat, Wasserstoffperoxyd, Bleidioxyd und Chloramin B, nach der Jodmonochlorid-Methode verwendet. Der Überschuss an Kaliumjodid der zu jeder dieser Substanzen zugegeben wurde, wird in saurem Milieu mit einer Titerlösung von Cer(IV)di(äthylendiamin)sulfat titriert. Das Chloroform wird als Indikator verwendet. Es färbt sich violett durch das während der Titration in Freiheit gesetzte Jod und wird am Endpunkt durch die Bildung von Jodmonochlorid blassgelb.

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THE TITRATION OF NICKEL WITH EDTA AT pH 2.8

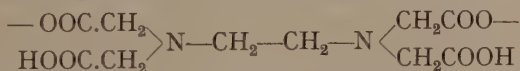
by

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INTRODUCTION

In the present article the titration of nickel with EDTA (ethylenediaminetetraacetate) which can be regarded as a complex H_2Y^{-2} , where Y represents



at pH 2.8 is described, in which use is made of the reaction between EDTA and thorium¹.

A small excess of EDTA is added to the nickel-containing solution, the pH is adjusted to about 2.8 and the excess is back-titrated with thorium nitrate, using alizarin-S as indicator.

SCHWARZENBACH and co-workers have determined the complex-forming constants of a number of elements². For nickel they give

$$K_1 = \frac{(Ni^{+2}) (Y^{-4})}{(NiY^{-2})} = 10^{-18.45} \text{ at } 20^\circ \text{C.}$$

It is calculated from this that at pH 2.8, less than 0.1% of nickel is present as free ion, when equivalent quantities of Ni^{+2} and H_4Y are present.

The titration of nickel in the manner described above is thus highly feasible. The results may be expected to be somewhat low, since during the titration with thorium nitrate the secondary reaction $NiY^{-2} + Th^{+4} \rightleftharpoons ThY + Ni^{+2}$ will also take place to some slight extent (the complex-formation of ThY is greater than that of NiY^{-2} , see below); but these exchange reactions appear to take place slowly, since our experiments have shown that any error due to them is small.

The nickel complex formed is blue in colour. We availed ourselves of this property for the rough spectrophotometric determination of the complex-forming constant of thorium with EDTA. Known quantities of nickel, thorium and EDTA were brought together, and the decrease in extinction measured; this at once shows that complex formation is greater with thorium than with nickel.

An advantage offered by the titration method is that it can be performed in the presence of cobalt. Quantities of Co up to 10 mg interfered hardly at all, so that the method permits the direct determination of nickel in the presence of cobalt.

EXPERIMENTAL PART

Reagents

All reagents were of c.p. grade. Deionized water (spec. resistance $> 10^6$ ohm) was used in the experiments. For the nickel determinations a nickel nitrate solution was used, the content of which had been determined gravimetrically as Ni-dimethylglyoxime.

The content was checked by

1. titration with EDTA for murexide at pH 11.5

2. acidimetrically after passage through a cation exchanger in H^+ form.

The maximum deviation in respect of the gravimetric method amounted to \pm or -0.20% .

EDTA solution 0.05M:

Dissolve 18.6 g of ethylene diamine tetraacetic acid (disodium salt) and dilute to 1000 ml.

Thorium nitrate solution 0.05M:

Dissolve 27.6 g of $Th(NO_3)_4 \cdot 4H_2O$ and dilute to 1000 ml. Both solutions are standardized by the method described in¹.

Alizarin-S indicator, 0.1%:

Dissolve 0.1 g of alizarin-S and dilute to 100 ml.

Monochloroacetic acid 2M:

Dissolve 189 g of $CH_2ClCOOH$ and dilute to 1000 ml.

Sodium acetate 1M:

Dissolve 136 g of $CH_3COONa \cdot 3H_2O$ and dilute to 1000 ml.

Method

A small excess (1-5 ml) of EDTA solution is added to the solution containing 1-4 m equiv. of Ni (30-120 mg). The solution is diluted to about 100 ml and neutralized with ammonia 2N against Congo red paper. 5 ml monochloroacetic acid solution and 5 ml sodium acetate solution are then added. The pH is checked and, if necessary, adjusted with ammonia or HCl 2N (pH limits 2.7-2.9).

1.5 ml of alizarin-S indicator solution are added, and immediately afterwards the excess of EDTA is back-titrated with thorium nitrate solution; the colour change from green to brown is very sharp.

A number of the values found by this method are reproduced in Table I.

TABLE I

TITRATION OF Ni WITH AN EXCESS OF EDTA AND BACK-TITRATION WITH THORIUM NITRATE AT pH 2.8

Ni present mg	Ni found mg	Deviation in mg
17.57	17.41	-0.16
	17.45	-0.12
35.14	35.14	0
52.71	52.72	+0.01
	52.72	+0.01
70.28	70.03	-0.25
	70.25	-0.03
99.4	99.3	-0.1
	99.7	+0.3

Influence of the pH

Good results were obtained in a pH interval varying from 2.6-4.3; at the latter pH (at which the titration is performed at the boiling temperature, see¹, the values for nickel lie 0-0.2% above the expected value.

A pH of 2.8 was selected, however, since then Mn and Co exert no influence. This is of importance in the analysis of steel.

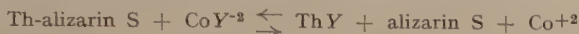
Influence of excess of EDTA

A 10-50% excess of EDTA has no influence on the results, provided that during the back-titration the pH does not fall below 2.7.

The quantity of buffer solution has been chosen so that at an excess of 1 m equiv. of EDTA (0.5 mmol) the pH does not appreciably change during the back-titration with thorium nitrate.

Influence of other metal ions

Special attention was paid to the influence of cobalt, since the latter often occurs in combination with nickel. It appeared that even 10-20 mg of Co in combination with 100 mg of Ni produced only a slight (0.5-1%) excess value for nickel. The colour change is somewhat hesitant in this case, because the end-colour continuously recedes due to the exchange reaction



The end-point is clearly perceptible, however, as a permanent colour change to brown.

In the presence of Co it is advisable to increase the volume of the solution to 175-200 ml; moreover additional indicator should be added (2.5 ml instead of 1.5 ml). The values given in Table II were determined in this way.

TABLE II

NICKEL WITH EXCESS EDTA AND BACK-TITRATION WITH THORIUM NITRATE IN THE PRESENCE OF Co (pH 2.6-2.8, VOLUME 175-200 ml, 2.5 ml INDICATOR SOLUTION)

mg Ni present	mg Ni found	Deviation mg Ni	Further data	
72.87	72.21	-0.66	5 mg Co	pH 2.6
	72.57	-0.30	"	pH 2.7
	72.69	-0.18	"	pH 2.8
	72.93	+0.06	"	"
	73.11	+0.24	10 mg Co	"
101.6	102.1	+0.5	"	"
	102.0	+0.4	"	"
	102.4	+0.8	20 mg Co	"
	102.2	+0.6	"	"

Although in the table only cobalt quantities of up to only 20 mg are cited, we have also made tests with up to 50 mg of Co in combination with 100 mg Ni. The deviations are then greater (2% relatively) and the determination of the end-point is rather difficult.

The fact that Co^{+2} affects the nickel titration to only a small extent must be attributed to its weaker tendency to complex-formation as compared with nickel ($K_{\text{CoY}^{-2}} = 10^{-16.1}$, $K_{\text{NiY}^{-2}} = 10^{-18.45}$) whilst the great binding tendency of thorium to EDTA ($K_{\text{ThY}} \approx 10^{-19.8}$) may also have a favourable influence.

Accordingly the influence of 10 mg of Zn ($K_{\text{ZnY}^{-2}} = 10^{-16.15}$) is of the same order as that of Co. For 10 mg of Mn ($K_{\text{MnY}^{-2}} = 10^{-13.5}$) the influence is nil, as would be expected.

The influence of Pb, however, ($K_{\text{PbY}^{-2}} = 10^{-18.2}$) is fairly considerable. In the presence of 5 mg of Co, Zn and Pb in combination with 100 mg Ni for example, we found a 1% higher result, whilst in the presence of 50 mg of Zn and Pb the end-point could not even be distinctly determined,

Cu^{+2} ($K_{\text{CuY}^{-2}} = 10^{-18.38}$) reacts for 95% just as Al, whilst Fe^{+3} ($K_{\text{FeY}^{-2}} = 10^{-25.1}$) reacts quantitatively, just as Bi^{+3} ($K_{\text{BiY}^{-2}} ?$).

Ca, Ba, Sr and Mg in quantities of 40 mg do not interfere (K greater than 10^{-11}).

For the influence of anions we refer the reader to a previous publication³.

APPROXIMATE DETERMINATION OF THE COMPLEX-FORMING CONSTANT OF THORIUM WITH EDTA

The blue colour of the nickel complex was used to determine an approximate value for the complex-forming constant of Th-EDTA.

The principle was as follows:

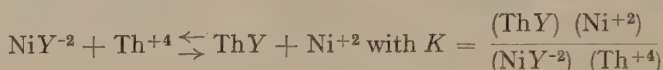
Equivalent quantities of Ni and EDTA were brought together and varying quantities of thorium nitrate added. The pH was adjusted at 2.5-3.0, the solution made

0.1N to KCl and the whole diluted to 100 ml. The extinctions of the solutions thus obtained were measured after 12 hours' standing (the extinctions had then become constant, showing that equilibrium had been reached).

From the change in extinction the (NiY^{-2}) could at once be determined, whilst the other concentrations could be calculated from the initial situation and the (NiY^{-2}) .

With the help of $K_{\text{NiY}^{-2}} = 10^{-18.45}$ the value of K_{ThY} was then found.

It was assumed in the calculation that the formation of NiY^{-2} and ThY goes to completion; this is permissible in view of the very strong complex formation. The reaction, in which we were interested, can then be schematically represented by (a):



and the latter reaction can be imagined to be composed of (b):



and (c):



so that $K = \frac{K_{\text{NiY}^{-2}}}{K_{\text{ThY}}}$ and consequently $\log K_{\text{ThY}} = \log K_{\text{NiY}^{-2}} - \log K$

(NiY^{-2}) was calculated directly as the proportion of the extinctions of the equilibrium- and initial conditions, E_e and E_s respectively, multiplied by the initial concentration of NiY^{-2} ($=C_{\text{NiY}^{-2}}$). A small correction on E_e was carried out, because the Ni^{+2} liberated also absorbs slightly at the wavelength used. This correction was easily calculated from the extinction of a pure Ni^{+2} solution (see Table III).

It follows further from reaction (a):

$$(\text{Ni}^{+2}) = C_{\text{NiY}^{-2}} - (\text{NiY}^{-2})$$

$$(\text{ThY}) = (\text{Ni}^{+2})$$

$$(\text{Th}^{+4}) = C_{\text{Th}^{+4}} - (\text{ThY}) \text{ (in which } C_{\text{Th}^{+4}} \text{ is the added quantity of } \text{Th}^{+4}\text{).}$$

TABLE III

EXTINCTION OF SOLUTIONS WITH EQUIVALENT QUANTITIES Ni^{+2} AND EDTA WITH VARYING QUANTITIES OF Th^{+4}

Milieu 0.1N KCl, pH 2.5-3, volume 100 ml. Temp. ca. 20° C. Wavelength 600 mμ, cell 30 mm

E_s	E_e	$E_e \text{ (corr.)}$	$C_{\text{Th}^{+4}}$	(NiY^{-2})	(Ni^{+2})	(Th^{+4})	K
	0.340	0.334	$0.3395 \cdot 10^{-2}$	$1.358 \cdot 10^{-3}$	$0.337 \cdot 10^{-2}$	$0.0025 \cdot 10^{-2}$	33.4
	0.271	0.260	$0.6790 \cdot 10^{-2}$	$1.057 \cdot 10^{-2}$	$0.638 \cdot 10^{-2}$	$0.041 \cdot 10^{-2}$	9.4
	0.185	0.168	$1.0185 \cdot 10^{-2}$	$0.683 \cdot 10^{-2}$	$1.012 \cdot 10^{-2}$	$0.0065 \cdot 10^{-2}$	23.1
	0.109	0.087	$1.3580 \cdot 10^{-2}$	$0.354 \cdot 10^{-2}$	$1.341 \cdot 10^{-2}$	$0.017 \cdot 10^{-2}$	29.8
0.417	1.695 $\cdot 10^{-2}$ mol Ni^{+2} /l and 1.695 $\cdot 10^{-2}$ mol EDTA/l						
0.000	1.358 $\cdot 10^{-2}$ mol Th^{+4} /l and 1.695 $\cdot 10^{-2}$ mol EDTA/l						
0.030	1.695 $\cdot 10^{-2}$ mol Ni^{+2} /l in 0.1N KCl.						

From the K values thus found we calculate for $\log K_{\text{ThY}}$:

— 18.45 — 1.52 = — 19.97	to 1 place of decimals	— 20.0
— 18.45 — 0.97 = — 19.42	„ „ „	— 19.4
— 18.45 — 1.36 = — 19.81	„ „ „	— 19.8
— 18.45 — 1.47 = — 19.92	„ „ „	— 19.9
average		— 19.8 \pm 0.13

$$K_{\text{ThY}} = 10^{-19.8 \pm 0.13}$$

SUMMARY

A method for determining nickel using EDTA is described. A small excess of EDTA is added, the pH adjusted to 2.7-2.9 and the solution back-titrated with thorium nitrate, against alizarin-S as indicator. Quantities of cobalt up to 10 mg do not interfere.

In addition an approximate determination of the complex-forming constant of Th-EDTA is described, based on the decrease in extinction of an Ni-EDTA solution to which Th^{+4} has been added.

RÉSUMÉ

Une méthode est décrite pour le dosage du nickel au moyen de l'acide éthylènediaminotétracétique (EDTA). Un léger excès de réactif est ajouté, le pH est ajusté à 2.7-2.9 et la solution est titrée en retour par le nitrate de thorium, en présence d'alizarine-S comme indicateur. Des quantités de cobalt allant jusqu'à 10 mg ne gênent pas. On décrit également une détermination approximative de la constante de formation du complexe Th EDTA, basée sur la diminution de l'extinction d'une solution Ni-EDTA à laquelle on ajoute Th^{+4} .

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben, um Nickel mittels der Äthylendiaminotetraessigsäure (EDTA) zu bestimmen. Ein leichter Überschuss des Reagenzes wird zugegeben, der pH auf 2.7-2.9 gebracht und die Lösung in Gegenwart von Alizarin-S als Indikator mit Thoriumnitrat zurücktitriert. Kobaltmengen bis zu 10 mg stören nicht. Beschrieben wird ebenfalls eine annähernde Bestimmung der Th-EDTA-Komplexbildungs-Konstante, welche auf der Verminderung der Extinktion einer Ni-EDTA-Lösung beruht, zu welcher man Th^{+4} zufügt.

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THE DETERMINATION OF ZIRCONIUM IN FLUORIDE-CONTAINING SOLUTIONS

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INTRODUCTION

The recently developed EDTA titration procedures for zirconium have proved extremely useful in the analysis of binary alloy systems. Thus the direct titration of zirconium is possible in the analysis of uranium-zirconium¹ and cerium-zirconium alloys². With tantalum-zirconium and niobium-zirconium alloys the separation of the zirconium from the earth acid constituent was found to be desirable³. This was accomplished by the solvent extraction of most of the earth acid element into hexone from a fluoride solution of the sample. The zirconium was finally separated from small amounts of unextracted tantalum or niobium by precipitation with ammonium hydroxide in the presence of hydrogen peroxide, the earth acid elements remaining in solution as peroxy complexes under these conditions. In the analysis of ternary alloy systems for zirconium by the EDTA procedure, the preliminary separation of the zirconium from other alloying constituents appeared desirable. A technique was required that was reasonably specific for zirconium and was also directly applicable to fluoride-containing solutions. This latter requirement arose because of the need to use hydrofluoric acid in effecting the complete solution of zirconium-containing alloys.

Zirconium can be readily precipitated from fluoride solutions as insoluble barium fluozirconate. This precipitation was first employed by HUME⁴ in the analysis of fission products and TELFORD⁵ later used this technique in the analysis of uranium-niobium-zirconium alloys. In this latter work, zirconium in the range 50 to 150 mg was precipitated as barium fluozirconate and separated by filtration on a Whatman No. 42 filter paper. This precipitate was redissolved in a mixture of boric and hydrochloric acids, the zirconium being recovered from solution by precipitation with cupferron. After filtration, the cupferride precipitate was finally ignited to zirconium oxide. It is assumed that TELFORD took sample weights containing more than 50 mg of zirconium to give reasonable amounts of zirconium oxide to weigh at the end of the determination. This precipitation technique appeared very suitable for the preliminary separation of zirconium in complex alloy analysis before the application of the EDTA titration. Moreover, the use of the volumetric procedure

would eliminate the need to take sample weights containing more than 50 mg of zirconium, since it is readily applicable to amounts of zirconium of the order of a few milligrams. However, information was needed on the optimum solution conditions for the quantitative precipitation of the zirconium and on the behaviour of other elements in this process, although TELFORD's work showed conclusively that uranium and niobium do not interfere. Data on these points have been obtained in our study and are reported in this paper.

EXPERIMENTAL

The solvent acids needed for the solution of most ternary alloys can be expected to be hydrofluoric, nitric and hydrochloric acids in various combinations. In preliminary experiments therefore the precipitation of barium fluozirconate was studied from $\text{HNO}_3 + \text{HF}$ and $\text{HCl} + \text{HF}$ mixtures. Sulphuric acid clearly could not be used as a solvent acid in this work because of the simultaneous precipitation of barium sulphate with barium fluozirconate. In the precipitation experiments from nitric acid solutions, a suitable volume of a standard zirconyl nitrate solution was placed in a transparent plastic centrifuge tube together with a measured volume of nitric acid (sp.gr. 1.42) and the solution was diluted with water to a volume of 20 ml. Then 10 ml of a 5% w/v barium nitrate solution was added, followed by 2 ml of hydrofluoric acid (40%) with stirring. After centrifuging for 5 minutes, the completion of precipitation was tested by the addition of further small quantities of barium nitrate and hydrofluoric acid, followed by further centrifuging if necessary. The supernatant liquid was removed by means of a polythene suction line over the end of which a small piece of filter paper was held in position by a polythene ring. Any precipitate adhering to the paper was simply removed by washing.

The precipitate was then transferred quantitatively to a beaker containing 10 ml of hydrochloric acid (sp.gr. 1.16), 10 ml of 5% boric acid and 75 ml of water. After boiling for 10-15 minutes the solution was returned to the centrifuge tube and made alkaline by the addition of ammonium hydroxide. The zirconium hydroxide precipitate was recovered by centrifuging, dissolving in a small amount of hydrochloric acid (1+1) and then evaporating to fumes of 20 ml of perchloric acid (60%) to ensure the complete removal of fluoride ions. The zirconium was then determined volumetrically by the addition of a slight excess of EDTA and back titrating at pH 5 to 6 with a standard iron solution, using salicylate as the indicator. Quantitative recoveries were obtained for zirconium from solutions up to 3N in nitric acid at the precipitation stage, whereas slightly low figures were obtained from solutions 5N in nitric acid. Typical results for the recovery of zirconium in amounts up to 100 mg are given in Table I.

TABLE I

RECOVERY OF ZIRCONIUM FROM NITRIC ACID SOLUTIONS

Normality of nitric acid in solution	Wt of zirconium taken (mg)	Wt of zirconium recovered (mg)
5.0	3.9	3.0
3.0	3.9	4.0
1.0	3.9	4.0
1.0	10.0	10.1
1.0	19.9	19.8
1.0	39.9	39.95
1.0	59.8	59.75
1.0	99.7	99.2

The above experiments were repeated in hydrochloric acid solutions, using barium chloride instead of the barium nitrate solution. The results in Table II show that the precipitation of barium fluozirconate is equally effective in hydrochloric acid media, complete recoveries being obtained from acid concentrations up to at least 3N.

TABLE II
RECOVERY OF ZIRCONIUM FROM HYDROCHLORIC ACID SOLUTIONS

Normality of hydrochloric acid	Wt of zirconium taken (mg)	Wt of zirconium recovered (mg)
0.5	20.0	20.1
1.0	20.0	19.9
3.0	20.0	20.1
5.0	20.0	19.7
7.5	20.0	Low and erratic recoveries

The barium fluozirconate precipitates were not washed in the above investigation. This process was purposely omitted because the experiments were carried out on pure zirconium solutions. With alloy solutions, however, it was necessary to wash the zirconium precipitates and work was therefore undertaken to develop a suitable washing technique. TELFORD simply washed the barium fluozirconate precipitates with water, but our experience showed that slight loss of zirconium could occur. We obtained better results by using a wash solution 1% w/v in barium nitrate, 2% v/v in hydrofluoric acid and 10% v/v in nitric acid, the composition of this solution approximately simulating that of the supernate. The wash solution finally chosen for this work had also been in contact with barium fluozirconate. A small amount of zirconium was included in the preparation of the solution and the precipitated barium fluozirconate was removed by filtration before use.

THE BEHAVIOUR OF OTHER ELEMENTS IN THE BARIUM FLUOZIRCONATE PRECIPITATION

Details are given here of the behaviour of other elements in the zirconium procedure. High purity zirconium metal (0.04% Hf by spectrographic analysis) was used throughout. This investigation was limited, however, to metals normally used in non-ferrous alloy systems. In some cases, where the other constituent was known to react with EDTA under the conditions for the titration of zirconium, a double precipitation of the latter was undertaken. To enable this second precipitation to be carried out, the first barium fluozirconate precipitate from solutions 2M in HF and less than 3M in HNO₃ was dissolved with stirring in 2 to 3 ml of saturated boric acid and about 10 ml of hot 20% nitric acid. This solution was diluted to 20 ml with water and the second precipitation of barium fluozirconate effected by the addition of 10 ml of 5% barium nitrate and 2 to 3 ml of hydrofluoric acid. In this study a recently improved procedure⁶ for zirconium was also substituted for the visual method using salicylic acid as the indicator. In this method the titration of the excess of EDTA is carried out at pH 2.3 and a photoelectric absorptiometer is used to determine the end-point.

a) Niobium and tantalum

Specpure niobium metal and tantalum metallic sheet of 99.9% purity was used in this work, weighed amounts being dissolved in a few ml of (1+1) nitric acid by the dropwise addition of hydrofluoric acid. After the transference of these solutions to plastic centrifuge tubes, measured amounts of a gravimetrically standardized zirconyl nitrate solution were added. These solutions were then treated with barium nitrate and hydrofluoric acid to effect precipitation of barium fluozirconate. On re-solution in nitric-boric acids after a single precipitation, turbidities were often produced due to the hydrolysis of small amounts of co-precipitated niobium or

tantalum. The addition of 1 or 2 drops of hydrogen peroxide (100 vols.) readily removed this cloudiness before the re-precipitation of the barium fluozirconate was carried out. The results obtained for the determination of 21.9 mg amounts of zirconium in the presence of varying amounts of niobium and tantalum up to a maximum of 1 g are given in Table III. Under these conditions there is clearly no interference from the earth acid elements.

TABLE III

DETERMINATION OF ZIRCONIUM IN THE PRESENCE OF NIOBIUM OR TANTALUM

Wt of Zr taken (mg)	Wt of earth acids taken (mg)	Wt of Zr recovered (mg)
21.9	250 Nb	22.1
21.9	500 Nb	22.1
21.9	1,000 Nb	22.0
21.9	250 Ta	22.0
21.9	500 Ta	21.9
21.9	1,000 Ta	22.0

b) Tungsten

Tungsten metal of 99.9% purity was dissolved in nitric-hydrofluoric acids for these tests. On re-solution of the barium fluozirconate in nitric-boric acids, a small yellow precipitate of tungstic acid was sometimes visible, especially in the separation of small amounts of zirconium from large amounts of tungsten. A little tungstic acid sometimes passed through to the final solution prior to titration. In these cases, the precipitate was removed by centrifuging and it was also washed with hydrochloric acid. The supernate and washes were combined and evaporated to fumes of perchloric acid in the ordinary way before carrying out the titration. The non-interference of tungsten was confirmed in this work; in a typical experiment 49.4 mg of zirconium were combined with 1 g of tungsten and a zirconium recovery of 49.5 mg was obtained.

c) Titanium, uranium, molybdenum, lead, iron and copper

The recovery of 20 mg and other amounts of zirconium in the presence of amounts up to 1 g of lead, copper, iron and uranium showed that no serious difficulties arose from these elements. In the experiments with molybdenum and titanium, the maximum amount taken of each element was 500 mg and 850 mg respectively. No interference was encountered and no trouble is envisaged from the presence of larger quantities. Results are given in Table IV.

d) Aluminium and bismuth

Although aluminium forms strong soluble fluoride complexes, an insoluble precipitate was formed in the presence of barium ions. Bismuth also precipitated from solution, presumably as its oxyfluoride, when the amount of bismuth exceeded 50 mg in the 30 ml of solution needed for the precipitation of barium fluozirconate. Any bismuth accompanying the barium fluozirconate precipitate also consumes EDTA in the zirconium titration procedure and thereby leads to high results. The barium fluozirconate technique is therefore not suitable for the determination of zirconium in any alloy systems containing either bismuth or aluminium.

TABLE IV
DETERMINATION OF ZIRCONIUM IN THE PRESENCE OF Ti, U, Mo, Pb, Fe AND Cu

Wt of Zr taken (mg)	Wt of other constituent (mg)	Wt of Zr recovered (mg)
13.2	100 Ti	13.3
13.2	250 Ti	13.0
50.7	250 Ti	50.6
50.7	500 Ti	50.8
148.0	850 Ti	148.0
9.4	1000 U	9.1
39.9	1000 U	39.8
99.7	1000 U	99.8
12.5	500 U	12.3
19.0	500 U	18.9
64.1	116 U	64.3
5.0	500 Mo	5.0
31.1	500 Mo	30.6
15.8	87.5 Mo	16.0
21.2	1000 Pb	21.9
21.2	500 Pb	22.1
21.2	250 Pb	22.2
20.4	1000 Fe	21.4
20.4	500 Fe	21.5
20.4	250 Fe	21.6
20.0	1000 Cu	20.1
20.0	500 Cu	20.8
20.0	250 Cu	20.2

e) Tin

In this case the precipitation of the barium fluozirconate had to be carried out from hydrochloric acid solutions, nitric acid being completely unsuitable because of the formation of metastannic acid. Under these conditions it was also necessary to add 1 or 2 drops of hydrogen peroxide to inhibit the formation of a precipitate. The recovery of 20.0 mg amounts of zirconium from various quantities of tin up to a maximum of 1 g showed that there was no interference from this element. For example, zirconium recoveries of 20.3, 20.1 and 20.4 mg were obtained in the presence of 250, 500 and 1000 mg amounts of tin.

THE DETERMINATION OF ZIRCONIUM IN ALLOY SYSTEMS

The procedure outlined in the previous section has been used for the determination of zirconium in several uranium base ternary alloy systems. The alloys under investigation were uranium-titanium-zirconium, uranium-niobium-zirconium and uranium-molybdenum-zirconium. Solutions of these materials can be attained by the judicious use of nitric acid and small amounts of hydrofluoric acid. After evaporation to ensure the removal of most of the free mineral acid from the sample

solution, the barium fluozirconate precipitation procedure can be applied directly and the zirconium content determined volumetrically with EDTA. Details of the procedure applicable to alloy systems are as follows:

1. Apparatus

Platinum dishes *ca.* 3'' in diameter are needed for the solution of alloys and transparent plastic centrifuge tubes (60 ml capacity) for the precipitation of barium fluozirconate. The fluoride containing solutions are mixed with polythene rods 4 mm in diameter.

An Eel photoelectric absorptiometer is suitable for the back-titration of the excess EDTA with a standard iron solution.

2. Reagents

a) Wash Solution — prepare a solution 1% w/v barium nitrate, 2% v/v hydrofluoric acid and 10% v/v nitric acid. Add a zirconium nitrate solution containing a few milligrams of zirconium and allow the barium fluozirconate precipitate to settle. Filter the solution and store in a polythene bottle.

b) Iron solution (0.1M) — dissolve 5.585 g of "specpure" iron in 20 ml of warm hydrochloric acid (sp.gr. 1.16). Dilute with water and completely oxidize by the careful dropwise addition of nitric acid (sp.gr. 1.42). Dilute to 1 litre with water.

c) EDTA solution (0.1M) — dissolve 37.23 g of the disodium salt of ethylenediamine tetraacetic acid in water and dilute to 1 litre. Standardize this solution by accurately pipetting 25 ml into a 400 ml squat type beaker and diluting to a volume of about 300 ml with water. Adjust the pH of this solution to a value of 2.3 and position the beaker in the absorptiometer. Add 1 ml of a 2% potassium benzohydroxamate solution, stir the solution mechanically and adjust the absorptiometer reading to zero with Ilford 605 filters in position. Carry out the titration by addition of the standard iron solution from a calibrated burette, measuring the absorbancy at points before and after the end-point. Keep the glass electrode in the solution and re-adjust the pH to 2.3 from time to time throughout the titration. Plot a graph of the volume of iron solution added against absorbancy and determine the end-point from the intersection of the two straight line portions of the graph.

3. Procedure

Take a suitable weight of sample (approx. 1 g) in the form of drillings or millings in a *ca.* 3'' covered platinum dish. Attack with about 20 ml of warm nitric acid (1+1) and add a few drops of hydrofluoric acid to assist solution. If a complete solution is produced, evaporate to a volume of about 2 ml. With samples producing a greenish precipitate of uranium tetrafluoride, add a small quantity of perchloric acid and fume strongly to decompose the precipitate, reducing the volume of the solution to about 2 ml by evaporation as before.

Transfer the sample solution to a centrifuge tube with water, but keeping the volume down to 20 ml. Then add 10 ml of a 5% w/v barium nitrate solution and 2 ml of hydrofluoric acid (40%). Allow to stand for 5 to 10 minutes, before centrifuging. At this stage add a further two drops of hydrofluoric acid to test for the complete precipitation of the zirconium. Remove the supernate by the special polythene suction line with a piece of filter paper covering the end and held in position by a polythene ring. Wash any precipitate adhering to the paper back into the centrifuge tube with water. Add 10 ml of the wash solution to the centrifuge tube and break up the precipitate using a polythene rod. Re-centrifuge and remove the solution as before. Dissolve the precipitate in 2 to 3 ml of saturated boric acid and about 10 ml of hot 20% v/v nitric acid, stirring to assist solution.

Re-precipitate the barium fluozirconate by the addition of 10 ml of 5% barium nitrate solution and 2 to 3 ml of hydrofluoric acid (40%). Repeat the centrifuging and washing of this precipitate as before dissolving in the boric-nitric acid mixture. Dilute this solution with water to a volume of approximately 30 ml and make ammoniacal to precipitate zirconium hydroxide. Centrifuge and remove the supernate. Then using a stirring rod wash the precipitate with 10-15 ml of hot 2% ammonium chloride. Centrifuge and remove the supernatant liquor as before. Dissolve the precipitate in 10 ml of hot hydrochloric acid (1+1), transfer the solution to a 400 ml squat beaker and evaporate to fumes of 20 ml of perchloric acid (60%). After strong fuming for 5-10 minutes, cool and wash the sides of the beaker with water. Then repeat the fuming process to ensure the complete removal of fluoride ions.

Continue fuming to reduce the volume of perchloric acid to about 2 to 3 ml. Then dilute the

solution with 25 to 50 ml of water and add the slight excess of standard EDTA solution to complex the zirconium without delay. Dilute to a volume of 300 ml with water, adjust the pH to 2.3, add 1 ml of the 2% benzohydroxamate solution and carry out the back titration of the excess EDTA with the standard iron solution exactly as described in the procedure for the standardization of the EDTA solution. Maintain the glass electrode in the solution and readjust the pH from time to time during the titration as required. Calculate the zirconium content from the amount of EDTA consumed, 1 ml of 0.1M EDTA = 9.122 mg of Zr.

RESULTS AND CONCLUSIONS

The above procedure has been tested by applying it to the determination of the zirconium content of synthetic ternary uranium base alloys, including the uranium-molybdenum-zirconium, uranium-titanium-zirconium and uranium-niobium-zirconium systems. In the first system the molybdenum varied from 5 to 15%, the zirconium from 1 to 10%, whilst the uranium was always greater than 75%. Both the titanium and zirconium contents of the second system were in the range 1 to 15% and the uranium was greater than 85%. With the third type of alloys, the uranium was in the range 50 to 80%, whilst the niobium and zirconium varied from 1 to 40%. Synthetic solutions of these alloys were prepared by dissolving suitable amounts of the respective pure metals in nitric and hydrofluoric acids in platinum dishes. These solutions were evaporated to volumes of about 2 ml before transference to a centrifuge tube and precipitation of the barium fluozirconate. The recovery results for zirconium are given in Tables V, VI and VII and in all cases a good agreement is shown between the amount of zirconium taken and the amount finally recovered.

TABLE V

ANALYSIS OF SYNTHETIC URANIUM-MOLYBDENUM-ZIRCONIUM ALLOYS

Zirconium (%)	Wt of Zr taken (mg)	Uranium (approx. %)	Molybdenum (approx. %)	Wt of Zr in alloy by analysis (mg)	Zr in alloy by analysis %	Error in Zr determination %
1.1	10.9	84	15	10.8	1.1	nil
1.1	10.8	94	5	10.8	1.1	nil
5.0	49.8	85	10	49.3	4.9	-0.1
5.1	50.5	90	5	50.1	5.0	-0.1
9.9	49.5	82	8	49.1	9.8	-0.1
10.1	50.6	75	15	50.2	10.0	-0.1

TABLE VI

ANALYSIS OF SYNTHETIC URANIUM-TITANIUM-ZIRCONIUM ALLOYS

Zirconium %	Wt of Zr taken (mg)	Uranium (approx. %)	Titanium (approx. %)	Wt of Zr in alloy by analysis (mg)	Zr in alloy by analysis %	Error in Zr determination %
1.0	10.0	85	14	10.0	1.0	nil
4.1	20.4	86	10	20.7	4.1	nil
7.1	35.1	85	8	34.7	7.0	-0.1
7.3	36.3	85	8	36.0	7.2	-0.1
13.9	69.2	85	1	68.4	13.7	-0.2
14.4	72.1	85	1	71.7	14.3	-0.1

TABLE VII

ANALYSIS OF SYNTHETIC URANIUM-NIOBIUM-ZIRCONIUM ALLOYS

Zirconium (%)	Wt of Zr taken (mg)	Uranium (approx. %)	Niobium (approx. %)	Wt of Zr in alloy by analysis (mg)	Zr in alloy by analysis %	Error in Zr determination %
1.1	11.3	60	39	10.6	1.1	nil
10.1	50.3	80	10	50.3	10.1	nil
10.1	50.8	50	40	50.9	10.1	nil
15.2	76.1	65	20	76.1	15.2	nil
18.9	94.6	80	1	93.8	18.8	-0.1
25.0	100.1	50	25	99.4	24.8	-0.2
29.7	59.3	50	20	59.4	29.7	nil
38.9	77.6	60	1	77.2	38.7	-0.2

It can be concluded that the precipitation of zirconium as barium fluozirconate is a very useful technique for the separation of zirconium from other constituents in the analysis of uranium base alloys. After this separation, the ethylenediaminetetra-acetic acid procedure for zirconium is readily applicable with an appreciable saving in time when compared with the gravimetric method. Although the application of this new technique has been limited in this work to the analysis of uranium ternary base alloys, this procedure should help to simplify the determination of zirconium in other types of materials.

ACKNOWLEDGEMENT

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SUMMARY

In the recommended procedure the zirconium is first precipitated from solution as the insoluble barium fluozirconate. After separation, the precipitate is dissolved in a mixture of nitric and boric acids and the zirconium is then precipitated as its hydroxide. This precipitate is separated, dissolved in hydrochloric acid and this solution is evaporated to fumes of perchloric acid to remove completely fluoride ions. The zirconium content is then determined volumetrically by adding a slight excess of a standard solution of ethylenediaminetetra-acetic acid and back titrating with a standard iron solution at pH 2.3 using potassium benzohydroxamate as indicator and the photometric technique for end-point detection. This method is applicable to the determination of milligram amounts of zirconium in fluoride-containing nitric or hydrochloric acid solutions provided that the concentration of these acids is below 3*N*. It is also suitable for the determination of zirconium in the presence of any of the following elements — uranium, titanium, niobium, tantalum, molybdenum, tungsten, lead, iron, copper and tin.

RÉSUMÉ

Dans le procédé recommandé, le zirconium est d'abord précipité comme fluozirconate de baryum. Après séparation, le précipité est dissous dans un mélange d'acides nitrique et borique; le zirconium est ensuite reprécipité comme hydroxyde. Le précipité obtenu est séparé, dissous dans l'acide chlorhydrique, la solution est évaporée jusqu'à obtention des vapeurs d'acide perchlorique pour éliminer complètement les ions fluorhydriques. La teneur en zirconium est ensuite déterminée volumétriquement par addition d'un léger excès de solution étalon d'acide éthylène-diaminotétraacétique. L'excès est titré par une solution étalon de fer au pH 2.3, en utilisant le benzohydroxamate de potassium comme indicateur et la technique photométrique pour déterminer le point final. Cette méthode permet le dosage du zirconium dans des solutions d'acide nitrique ou chlorhydrique renfermant un fluorure, à condition que la concentration de ces acides soit inférieure à 3*N*. Elle permet également le dosage du zirconium en présence d'uranium, de titane, de niobium, de tantale, de molybdène, de tungstène, de plomb, de fer, de cuivre et d'étain.

ZUSAMMENFASSUNG

Im beschriebenen Verfahren wird Zirkonium zuerst als unlösliches Bariumfluorozirkonat gefällt. Nach der Abtrennung wird das Präzipitat in einer Mischung von Salpetersäure und Borsäure gelöst; dann wird das Zirkonium als Hydroxyd gefällt. Der erhaltene Niederschlag wird abgetrennt und in Salzsäure gelöst. Die Lösung wird bis zur Entwicklung von Perchlorsäurenebel verdampft um die Fluorionen vollständig zu vertreiben. Der Zirkonium-Gehalt wird dann volumetrisch durch Hinzufügen eines kleinen Überschusses einer eingestellten Äthylendiamintetraessigsäurelösung und nachheriger Rücktitration mit einer eingestellten Eisenlösung bei pH 2.3 und mit Kaliumbenzohydroxamat als Indikator bestimmt. Für die Bestimmung des Endpunktes wird die photometrische Technik angewendet. Die Methode wird für die Bestimmung von Milligrammengen von Zirkonium in Salpeter- oder Salzsäurelösungen, welche ausserdem Fluorid enthalten, angewendet. Die Konzentration der beiden Säuren muss unter $3N$ liegen. Die Methode eignet sich auch für die Bestimmung von Zirkonium in Anwesenheit der folgenden Elemente: Uran, Titan, Niob, Tantal, Molybdän, Wolfram, Blei, Eisen, Kupfer und Zinn.

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CERATE OXIDIMETRY

IV. OXIDATION OF CARBOHYDRATES

by

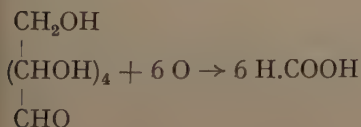
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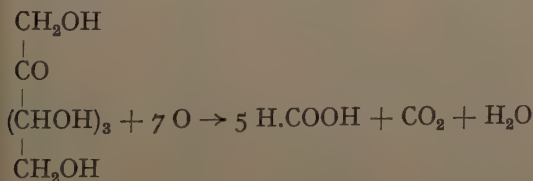
Several methods are available for the determination of reducing sugars including the classical Fehling and Benedict reagent methods, which are indirect and time-consuming. Another method, developed by WHITMOYER¹, involves the use of potassium ferricyanide. In this method, the reducing sugar is warmed with excess ferricyanide in sodium carbonate solution when an equivalent quantity of potassium ferrocyanide is produced. The solution is then acidified and the ferrocyanide titrated against standard ceric sulphate.

SMITH and co-workers² treated glucose with ceric perchlorate and found that it is oxidized to formic acid in 45 minutes, but the temperature of the reaction has to be controlled rather carefully.

Having studied the oxidizability of certain organic compounds with ceric sulphate^{3,4,5}, it was considered worth-while to study the action of ceric sulphate on reducing sugars. It has been found that the sugars containing the aldehydic group are oxidized to formic acid only:



In case of ketonic sugars also formic acid is the end-product but the ketonic group appears to be oxidized to carbon dioxide:



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Disaccharides are first hydrolysed to ketonic and aldehydic sugars. These hydrolysed products can be estimated as above.

MATERIALS

Ceric sulphate was prepared from ceric ammonium nitrate (B.D.H. AnalaR). The ceric hydroxide was precipitated from an aqueous solution of ceric ammonium nitrate by ammonia. The precipitate was washed thoroughly (by decantation), filtered and left overnight under suction. It was then dissolved in 5*N* sulphuric acid. (It has, however, been observed that exactly the same results are obtained even with a ceric sulphate solution prepared by dissolving the ceric ammonium nitrate directly in sulphuric acid of required strength.)

All other chemicals employed were either B.D.H. AnalaR or Merck products.

EXPERIMENTAL

A standard solution of the sugar was prepared directly by weight. Known volumes of this solution were mixed with ceric sulphate and the mixture refluxed for different intervals of time, the remaining excess of the ceric sulphate being determined as described earlier⁵. The results obtained are given in the following tables.

Observations with glucose

TABLE I

Vol. of glucose soln. ml	0.145 <i>N</i> Ce(SO ₄) ₂ ml	Refluxing time min	Ce(SO ₄) ₂ consumed ml	Equivalents of O ₂ consumed	Glucose found g	Glucose present g
2	5	5	2.42	10.52	0.00527	0.00600
2	5	10	2.68	11.65	0.00583	0.00600
2	5	15	2.74	11.97	0.00597	0.00600
2	5	30	2.73	11.91	0.00595	0.00600
2	5	60	2.74	11.97	0.00597	0.00600
2	5	120	2.74	11.97	0.00597	0.00600
3	5	10	3.81	11.05	0.00829	0.00900
3	5	15	4.03	11.73	0.00877	0.00900
3	5	20	4.11	11.98	0.00895	0.00900

The above data show that glucose is oxidized to formic acid within 15 minutes if about 100% excess of ceric sulphate is present. However, the time required for complete reaction increases if the excess of ceric sulphate is less.

Observations with fructose

TABLE II

Vol. of fructose soln. ml	0.145 <i>N</i> Ce(SO ₄) ₂ ml	Refluxing time min	Ce(SO ₄) ₂ consumed ml	Equivalents of O ₂ consumed	Fructose found g	Fructose present g
2	5	10	3.065	12.82	0.00572	0.00626
2	5	15	3.355	14.04	0.00626	0.00626
2	5	30	3.34	13.97	0.00623	0.00626
2	5	60	3.34	13.97	0.00623	0.00626
2	5	120	3.355	14.04	0.00626	0.00626
1	5	10	1.666	13.94	0.00311	0.00313
1	5	15	1.676	14.02	0.00313	0.00313

Results in the Table II show that 14 equivalents of oxygen are consumed per mole of the fructose oxidized. Carbon dioxide was also detected as one of the reaction products. The reaction, therefore, appears to proceed as follows.



Observations with sucrose

TABLE III

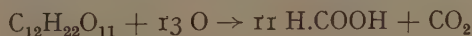
Vol. of sucrose soln. ml	0.1275N $\text{Ce}(\text{SO}_4)_2$ ml	Refluxing time min	$\text{Ce}(\text{SO}_4)_2$ consumed ml	Equivalents of O_2 consumed	Sucrose found g	Sucrose present g
2	5	5	2.49	24.70	0.00419	0.00442
2	5	10	2.61	25.89	0.00440	0.00442
2	5	15	2.61	25.89	0.00440	0.00442
2	5	30	2.60	25.80	0.00438	0.00442
2	5	60	2.61	25.89	0.00440	0.00442
2	5	135	2.61	25.89	0.00440	0.00442
3	5	10	2.51	16.50	0.00423	0.00663
3	5	20	3.69	24.41	0.00621	0.00663

Observations with lactose

TABLE IV

Vol. of lactose soln. ml	0.1275N $\text{Ce}(\text{SO}_4)_2$ ml	Refluxing time min	$\text{Ce}(\text{SO}_4)_2$ consumed ml	Equivalents of O_2 consumed	Lactose found g	Lactose present g
2	5	5	2.23	21.88	0.00375	0.00447
2	5	10	2.65	26.00	0.00446	0.00447
2	5	15	2.65	26.00	0.00446	0.00447
2	5	60	2.645	25.95	0.00445	0.00447
2	5	120	2.65	26.00	0.00446	0.00447
1	5	10	1.32	25.97	0.00222	0.00223
1	5	60	1.32	25.97	0.00222	0.00223
2	3	10	2.367	23.22	0.00398	0.00447
2	3	15	2.47	24.33	0.00416	0.00447

The data in Table III and IV show that in the presence of 100% excess of ceric sulphate, sucrose and lactose are both oxidized to formic acid according to the equation.

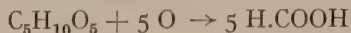


Observations with xylose

TABLE V

Vol. of xylose soln. ml	0.1254N $\text{Ce}(\text{SO}_4)_2$ ml	Refluxing time min	$\text{Ce}(\text{SO}_4)_2$ consumed ml	Equivalents of O_2 consumed	Xylose found g	Xylose present g
2	5	10	3.10	9.91	0.00584	0.00585
2	5	15	3.11	10.00	0.00585	0.00585
2	5	30	3.11	10.00	0.00585	0.00585
2	5	60	3.11	10.00	0.00585	0.00585

The above table shows that xylose is oxidized to formic acid within 10 minutes



ACKNOWLEDGEMENT

My sincere thanks are to Dr. R. C. MEHROTRA, Reader in Chemistry, University of Lucknow, for his valuable guidance throughout the progress of this work.

SUMMARY

It has been shown that glucose and xylose are oxidized completely to formic acid with ceric sulphate and require respectively 12 and 10 equivalents of oxygen per gram mole of the sugar.

Under the same conditions, fructose requires 14 equivalents of oxygen per gram mole and in this case, the ketonic group is further oxidized to carbon dioxide.

The disaccharides can be estimated by the above procedure after hydrolysis.

RÉSUMÉ

Il est démontré que le glucose et le xylose peuvent être oxydés quantitativement en acide formique, au moyen de sulfate de cérium (IV), ce qui nécessite respectivement 12 et 10 équivalents d'oxygène par molécule-gramme de sucre.

Dans les mêmes conditions, le fructose exige 14 équivalents d'oxygène par molécule-gramme, et dans ce cas, le groupe cétonique est encore oxydé en anhydride carbonique.

Les disaccharides peuvent être dosés par le procédé décrit, après hydrolyse.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass Glykose und Xylose durch Cer(IV)-sulfat vollständig zu Ameisensäure oxydiert werden. Für 1 Grammole der beiden aufgeführten Zucker werden 12 respektive 10 Äquivalente Sauerstoff gebraucht.

Unter den gleichen Bedingungen verbraucht Fruktose 14 Äquivalente Sauerstoff pro Grammole. In diesem Falle wird die Ketogruppe weiter zu Kohlendioxyd oxydiert.

Disaccharide können nach erfolgter Hydrolyse nach dem beschriebenen Verfahren bestimmt werden.

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5:6-BENZOQUINALDINIC ACID AS AN ANALYTICAL REAGENT II. DETERMINATION OF TITANIUM

by

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In a previous communication¹ it was shown that the reagent 5:6-benzoquinaldinic acid could be used for the separation and determination of quite a large number of elements. This paper deals with the use of the reagent for the estimation of titanium and its separation from rare earths, alkaline earths, magnesium, thorium, zirconium and iron.

Titanium in the tetravalent state is completely precipitated at and above pH 3.0 and its separation from rare earths has been effected at a pH between 3.0 and 5.0. Ammonium salts help to keep the alkaline earths and magnesium in solution. The titanium complex with the reagent is never found to be of definite composition and hence, before weighing, it is ignited to the oxide.

PŘIBIL and his co-workers² separated titanium(IV) from iron(III) and aluminium by precipitation as hydroxide in presence of the disodium salt of ethylenediamine-tetraacetic acid (complexone III). PICKERING³ observed that the precipitation of titanium as the hydroxide in the presence of complexone was a slow process and so used a magnesium salt as a demasking agent for the quick and effective separation of small quantities of titanium.

Complexone forms a much more stable complex with magnesium than with titanium, which again forms a 5:6-benzoquinaldinic acid complex much less soluble than the magnesium benzoquinaldinate. The magnesium salt then acting as a demasking agent assists in the precipitation of titanium by the reagent in the presence of complexone. If the procedure is carried out with sufficient ammonium salt in solution to prevent precipitation of the magnesium, a good separation from thorium, zirconium and iron(III) can be readily accomplished. Aluminium is partially coprecipitated with the titanium during separation.

EXPERIMENTAL

Reagents and apparatus

Standard titanium solution was prepared from potassium titanium oxalate which was fumed with concentrated sulphuric acid containing ammonium sulphate. The solution was diluted and the titanium content standardized gravimetrically as the oxide.

A 1% alcoholic solution of 5:6-benzoquinaldinic acid, crystallized from glacial acetic acid and of m.p. 187° C, was used as the precipitant. All other chemicals used were of reagent quality.

References p. 429.

Standard solutions used were prepared from reagent grade chemicals and their strengths were determined gravimetrically excepting that of calcium which was determined volumetrically.

A Cambridge bench model pH-meter was used for measurements of pH.

Procedure

Determination of titanium. The solution of titanium ($\text{TiO}_2 = 27.6 \text{ mg}$) was diluted to 250 ml and to it was added a slight excess of the reagent. After heating the solution to boiling the pH was brought to the required value by dropwise addition of 2N ammonium hydroxide solution. The solution was left on a hot plate for 20-30 minutes and filtered, washed with hot 1% ammonium nitrate solution, dried and then ignited to TiO_2 before weighing (see Table I).

TABLE I

pH	TiO_2 found mg	Error mg
4.0	27.7	+0.1
3.5	27.6	0.0
3.0	27.7	+0.1
2.7	27.4	-0.2
2.5	27.0	-0.6

Separation from alkaline earths, rare earths and magnesium. Separation from rare earths, alkaline earths and magnesium was carried out by the procedure given above. The acidity was controlled by methyl orange, screened with indigo carmine, so that the pH was about 4 at the time of precipitation and the presence of ammonium chloride (5 g) helped to keep the magnesium and the alkaline earths in solution (see Table II).

TABLE II

Ions present mg	pH	TiO_2 found mg	Error mg
Mg ⁺ 2 —100	4.0	27.5	-0.1
" —100	4.0	27.6	0.0
Ca ⁺ 2 —100	4.1	27.7	+0.1
" —100	4.0	27.5	-0.1
Sr ⁺ 2 —100	4.05	27.6	0.0
" —100	4.0	27.5	-0.1
Ba ⁺ 2 —100	4.2	27.8	+0.2
" —100	4.0	27.5	-0.1
R ₂ O ₃ —100	4.0	27.7	+0.1
" —200	4.5	27.6	0.0
" —200	4.8	27.5	-0.1

Determination in the presence of thorium, zirconium or iron(III). The acid titanium solution containing thorium, zirconium or iron was treated in succession with about 10 g of ammonium chloride, a few ml of 10% complexone III solution, a few ml of magnesium sulphate (10 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml) solution, sufficient reagent solution for complete precipitation of the titanium, and a few drops of screened methyl orange, and was finally diluted to 250 ml. The solution was brought to the boil and treated with 2N ammonium hydroxide until the colour of the indicator just changed to green. The solution was kept on a hot plate for about fifteen minutes, filtered, washed with hot 1% ammonium nitrate solution, ignited and weighed as TiO_2 (see Table III).

The amount of complexone added depended on the quantity of the other elements present and that of magnesium sulphate on the amount of excess complexone present in solution. Large excess of magnesium sulphate should be avoided as it affected the results for titanium separation from iron.

Separation from aluminium was not possible as it coprecipitated with titanium.

References p. 429.

TABLE III

Foreign element present mg	10% Complexone ml	10% Magnesium sulphate ml	TiO ₂ found mg	Error mg
ZrO ₂ — 26.5	5	10	27.5	—0.1
„ — 53	10	15	27.6	0.0
ThO ₂ — 55.2	5	10	27.7	+0.1
„ — 100.4	10	15	27.5	—0.1
Fe+ ³ — 25	10	15	27.7	+0.1
„ — 100	20	20	27.5	—0.1
Al ₂ O ₃ — 25	10	15	37.2	+9.6

Further work on the determination and separation of other elements is in progress.

SUMMARY

The reagent 5 : 6-benzoquinaldinic acid precipitates titanium(IV) completely from solution at and above pH 3.0 in the presence of rare earths. Coprecipitation of magnesium and the alkaline earths is easily prevented by the addition of ammonium chloride. Separation from iron(III), thorium or zirconium can be carried out in the presence of complexone III, magnesium sulphate being used as a demasking agent. Separation from aluminium is not possible. The titanium precipitate is not of definite composition and so it is ignited to the oxide before weighing.

RÉSUMÉ

L'acide 5 : 6-benzoquinaldinique précipite quantitativement le titane(IV) en solution de pH 3 ou de pH plus grand, en présence des éléments des terres rares. La coprécipitation du magnésium et des éléments alcalino-terreux est facilement empêchée par addition de chlorure d'ammonium. La séparation du fer(III), du thorium et du zirconium peut s'effectuer au moyen du complexon III, le sulfate de magnésium étant ensuite utilisé comme réactif de „démasquage". La séparation de l'aluminium n'est pas possible. Le précipité de titane obtenu doit être calciné en oxyde avant la pesée, sa composition étant mal définie.

ZUSAMMENFASSUNG

Die 5 : 6-Benzochinaldinsäure fällt das Titan(IV) in einer Lösung von pH 3 oder höher in Gegenwart der seltenen Erden quantitativ aus. Die Kopräzipitation von Magnesium und der Erdalkalien kann durch Zugabe von Ammoniumchlorid leicht verhindert werden. Die Abtrennung von Eisen(III), Thorium und Zirkonium kann mittels Komplexon III ausgeführt werden. Das Magnesiumsulfat wird darauf als demaskierendes Reagenz gebraucht. Die Abtrennung vom Aluminium ist nicht möglich. Der erhaltene Titan-Niederschlag muss, bevor er gewogen wird, zum Oxyd kalziniert werden, da er nicht einheitlich ist.

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CONTRIBUTION AU DOSAGE CHIMIQUE DES MATIÈRES PLOMBIFÈRES

par

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INTRODUCTION

Dans le contrôle de certaines opérations métallurgiques importantes, il est utile et même souvent nécessaire de connaître les teneurs des produits en les principaux composés plombifères (oxyde de plomb, sulfate de plomb, sulfure de plomb, peroxyde de plomb, plomb métallique, silicate de plomb). Actuellement, les „méthodes” chimiques employées sont en fait des déterminations indirectes, obtenues généralement par différence à la suite de plusieurs dosages préalables. Il en résulte que les erreurs s'accumulent et que les résultats ne sont pas contrôlables.

Dans le but d'améliorer le contrôle de ces opérations, nous avons entrepris une étude détaillée du comportement chimique des composés plombifères normalement présents dans les minerais et les produits résultant du grillage de ces minerais. Nos essais ont tout d'abord porté sur les principaux composés, soit l'oxyde de plomb, le sulfure de plomb et le sulfate de plomb.

I. ÉTUDE DE L'OXYDE DE PLOMB, DU SULFURE DE PLOMB ET DU SULFATE DE PLOMB

A. POSITION DU PROBLÈME

Une méthode de dosage de l'oxyde de plomb, du sulfure de plomb et du sulfate de plomb est due à E. KROSSIN¹.

Sur trois prises différentes du produit à analyser, il détermine respectivement le plomb total, la somme (oxyde de plomb + sulfate de plomb) et l'oxyde de plomb. Pour cette dernière détermination l'oxyde de plomb contenu dans la matière à analyser est dissous sélectivement, mais le plomb n'est pas dosé dans la solution obtenue; seul est déterminé le plomb restant dans le résidu. La publication de E. KROSSIN n'expose que le principe des réactions sans préciser les détails opératoires.

Dans la méthode de KROSSIN, aucun composé n'est dosé par détermination directe et les teneurs en oxyde, sulfate et sulfure de plomb sont établies par différences. L'inconvénient majeur d'une telle méthode d'analyse est la proscription de toute vérification par un bilan; une erreur commise au cours d'une détermination influence

tous les résultats obtenus. En outre, la multiplication des prises d'essai diminue la précision de l'échantillonnage.

Il est donc utile de trouver une méthode permettant d'effectuer le dosage *direct* de chacun des composés.

B. ACTION DE L'ACÉTATE D'AMMONIUM

1. *Essais de dissolution*

L'acétate d'ammonium est un des réactifs les plus employés dans l'analyse chimique quantitative des matières plombifères. Il convient donc de commencer les recherches par l'étude de ce réactif.

Chaque échantillon à étudier est finement broyé (100 % de passé à 200 mesh soit une dimension de particule inférieure à 74 microns), séché et attaqué pendant 30 minutes par une solution chaude d'acétate d'ammonium à 50% (un poids d'acétate pour un poids d'eau distillée). La lixiviation, qui se fait avec agitation modérée, niveau constant, et ébullition constante, donne un filtrat et un résidu. Dans le filtrat chaud, on ajoute une solution d'acide sulfurique à 20% (un volume d'acide sulfurique concentré pour quatre volumes d'eau distillée) et on précipite ainsi le plomb sous forme de sulfate. Celui-ci est filtré, lavé, calciné et pesé.

Le résidu est redissous dans l'eau régale. La solution est évaporée et traitée par l'acide sulfurique et l'acétate d'ammonium et le plomb est déterminé par la gravimétrie du sulfate.

Avant de faire confiance aux poids de plomb dosés dans le filtrat et le résidu d'une lixiviation, il faut vérifier si leur somme permet de retrouver le plomb total contenu dans l'échantillon soumis à l'attaque.

Au cours de ces essais de dissolution, il faut également s'assurer que l'opération a effectivement dissous tout ce qui est soluble. Dans ce but, il suffit d'effectuer plusieurs attaques successives en renouvelant le réactif jusqu'à ce qu'une dernière attaque ne dissolve plus rien. Cette vérification finale doit être appliquée à chacun des essais de lixiviation exposés ci-dessous.

Dans ces conditions opératoires, sont entièrement solubles dans l'acétate d'ammonium, l'oxyde et le sulfate tandis que le sulfure de plomb est complètement insoluble.

2. *Dosage sélectif du plomb par la gravimétrie du sulfate*

Comme on vient de l'exposer, les composés de plomb dissous dans l'acétate d'ammonium sont donc précipités par l'acide sulfurique et dosés par la gravimétrie du sulfate. A première vue, le résultat peut être faussé par les composés solubles de calcium, de strontium et de baryum qui accompagnent le plomb dans la précipitation par l'acide sulfurique. (Ces composés solubles dans l'acétate d'ammonium sont notamment, nous l'avons vérifié, les oxydes de Ca, Sr, Ba et le CaSO_4 .) Nous avons constaté, par de nombreux déboires au cours des analyses, que ces éléments sont particulièrement gênants pour des solutions froides, riches en acide et riches en sels d'ammonium. Une étude des conditions de précipitation des sels de Pb, Ca, Ba, Sr et NH_4 nous a permis de déterminer des conditions opératoires dans lesquelles le sulfate de plomb est précipité sélectivement.

Dans ce procédé, les produits de l'attaque par l'acétate d'ammonium sont filtrés à chaud et la précipitation du plomb se fait alors en versant dans ce filtrat une solution chaude d'acide sulfurique à 20% (un volume d'acide sulfurique concentré pour quatre volumes d'eau distillée). L'addition d'un peu d'alcool méthylique après la réaction (acide sulfurique + solution d'acétate) permet de vérifier si la précipitation du plomb est complète.

La vérification de la présence de sels de Ca, Sr et Ba dans le nouveau filtrat a été faite, après refroidissement, par l'acide sulfurique ou l'oxalate d'ammonium. La présence de sels d'ammonium est également mise en relief par une ébullition suivie d'un refroidissement rapide.

Cette méthode assure la précipitation sélective du sulfate de plomb et présente

également l'avantage de diminuer le temps nécessaire à la formation d'un précipité séparable facilement par filtration. Appliquée chaque fois avant la filtration terminale du plomb, elle permet d'éliminer l'influence perturbatrice des alcalinoterreux.

C. ACTION DE L'ACIDE RICINOLÉIQUE

1. Aspect de la recherche

L'acide ricinoléique est le réactif utilisé par E. KROSSIN. Comme cet auteur ne donne pas de détails dans son article, nous avons dû élaborer le mode opératoire en surmontant de nombreuses difficultés. Nous exposons tout d'abord la méthode qui nous a permis de vérifier la conclusion de KROSSIN relative à la dissolution sélective de l'oxyde de plomb dans l'acide ricinoléique.

2. Principe des opérations

Le minerai est attaqué par de l'acide ricinoléique pur puis de l'alcool méthylique à une température voisine de 40° C. Après filtration sur un entonnoir chauffé, on obtient un résidu et un filtrat.

Le résidu est redissous par l'eau régale, puis précipité par l'acide sulfurique à l'état de sulfate de plomb. Ce sulfate est lavé, séché, calciné et pesé. Le filtrat est très difficile à analyser. Après avoir essayé un grand nombre de procédés, nous avons adopté la méthode suivante: élimination de l'alcool par évaporation, précipitation de l'acide sulfhydrique, reprise par acide nitrique et acide sulfurique et pesée à l'état de sulfate de plomb.

3. Détails du mode opératoire

On verse dans un vase de Berlin de 400 ml, forme basse, 50 g d'acide ricinoléique pur que l'on porte au bain-marie jusqu'à ce que l'acide ricinoléique soit bien limpide. A ce moment on ajoute petit à petit, tout en agitant constamment, une prise d'essai d'échantillon de 2 g. On laisse digérer pendant 4 heures en agitant de temps en temps. Vers la fin de cette opération, on chauffe de l'alcool méthylique le plus pur possible à une température voisine de 40° C. Au bout des 4 heures on laisse refroidir le mélange acide ricinoléique-composés plombifères pendant quelques minutes de telle façon qu'il ne prenne pas en masse, puis on ajoute 50 ml d'alcool méthylique pur et le reporte au bain-marie. Lorsque la solution est limpide, c'est-à-dire après une dizaine de minutes, on filtre sur un entonnoir chauffé. Cet entonnoir est chauffé, pendant toute la filtration, dans un dispositif analogue à un bain-marie dont on aurait enlevé une partie du fond. La filtration terminée, on lave le vase d'attaque à l'alcool chaud puis on filtre et lave jusqu'à élimination complète de la matière grasse. On obtient d'une part un résidu et d'autre part un filtrat.

4. Analyse du résidu

Le résidu est repris par 50 ml d'eau régale, puis évaporé presque à sec, repris par 20 ml d'acide sulfurique 50%. On évapore jusqu'à fumées blanches, reprend par l'eau, porte à l'ébullition pendant une dizaine de minutes et on laisse reposer pendant 12 heures. Après filtration, le précipité est lavé par l'acide sulfurique, puis à l'alcool pour éliminer les dernières traces d'acide sulfurique. Enfin, le précipité est séché à l'étuve à 100° pendant 3 heures, calciné à 550° pendant 45 minutes et pesé.

5. Analyse du filtrat

La solution alcoolique, contenant des composés gras, est assez difficile à analyser et c'est peut-être à cause de cette difficulté que E. KROSSIN dosait le plomb uniquement dans les résidus de lixiviations.

Après l'essai de plusieurs procédés, dont la saponification et l'électrolyse en milieu basique, nous avons adopté une méthode basée sur la précipitation par l'acide sulfhydrique et gravimétrie du sulfate.

Dans cette méthode, on chauffe le filtrat pour éliminer l'alcool, puis on y verse de l'hydroxyde de sodium en excès et on sature le milieu en H_2S . Après une décantation de trois heures, le résidu est repris par l'acide nitrique, puis par l'acide sulfurique et traité par la méthode de dosage gravimétrique du sulfate.

6. *Amélioration de la méthode*

La méthode qui vient d'être décrite présente quelques inconvénients de détail. En particulier, elle rend difficile le maintien de la température au cours de la lixiviation et donne lieu à des difficultés au cours de la filtration. Elle a été améliorée au cours des recherches. Ainsi les conditions de la lixiviation ont été modifiées en s'inspirant de la méthode qui venait d'être mise au point pour les composés zincifères².

L'échantillon est attaqué à chaud par un mélange d'alcool méthylique et d'acide ricinoléique. L'erlenmeyer contenant le mélange est surmonté d'un réfrigérant de Liebig et l'alcool condensé retombe dans le vase. La température est ainsi maintenue automatiquement aux environs de 66° C. Le remplacement de l'alcool méthylique par de l'alcool éthylique permet de travailler à 78° C.

Les détails sont exposés plus loin dans la méthode d'analyse moléculaire.

D. L'ANALYSE DE L'OXYDE DE PLOMB, DU SULFATE DE PLOMB ET DU SULFURE DE PLOMB

Les lixiviations des matières plombifères ont donc permis de dissoudre de manière sélective, d'une part l'oxyde de plomb dans l'acide ricinoléique et d'autre part le sulfate de plomb et l'oxyde de plomb dans l'acétate d'ammonium. Par ailleurs, il est bien connu, et nous l'avons vérifié une fois de plus, que le sulfure de plomb est complètement soluble dans l'acide nitrique.

Il ressort de ces essais un résultat pratique important: la possibilité de faire l'analyse moléculaire exacte d'un produit dans lequel les composés plombifères se réduisent à l'oxyde, le sulfate et le sulfure (cas fréquent dans la pratique).

Le Tableau I expose le schéma de la méthode proposée.

E. DESCRIPTION SUCCINCTE DU MODE OPÉRATOIRE

Prise d'essai: 5 g (poids sec) broyé à 200 mesh.

I. *Lixiviation dans l'acide ricinoléique*

La prise d'essai est introduite dans un petit erlenmeyer de 200 à 250 ml. Ajouter 10 ml d'alcool méthylique, agiter, puis ajouter 75 g d'acide ricinoléique chaud (60° C environ) et agiterdenouveau. Adapter alors à l'erlenmeyer un réfrigérant Liebig et chauffer l'erlenmeyer, avec précaution au début, jusqu'à l'ébullition. Les vapeurs d'alcool, condensées, retombent dans le vase et maintiennent la constance de la température.

A la fin de l'attaque, laisser refroidir quelque peu, enlever le réfrigérant Liebig, ajouter 100 ml d'alcool chaud et porter au bain-marie à une température d'environ 60° C pendant une dizaine de minutes (ne pas trop dépasser ce temps sinon l'alcool s'évapore et le milieu devient difficile à filtrer). La filtration se fait sur filtre chauffé au moyen d'un entonnoir plongeant dans un bain-marie dont le fond est perforé pour laisser passer la tige de l'entonnoir. Laver à l'alcool chaud.

La durée de l'attaque est variable. En général dans nos essais, la première attaque durait 8 heures et était suivie d'attaque de 2 heures jusqu'à constatation de l'absence de plomb dans le filtrat de la dernière attaque. Une attaque de 8 heures et deux attaques de 2 heures suffisaient dans la plupart des cas.

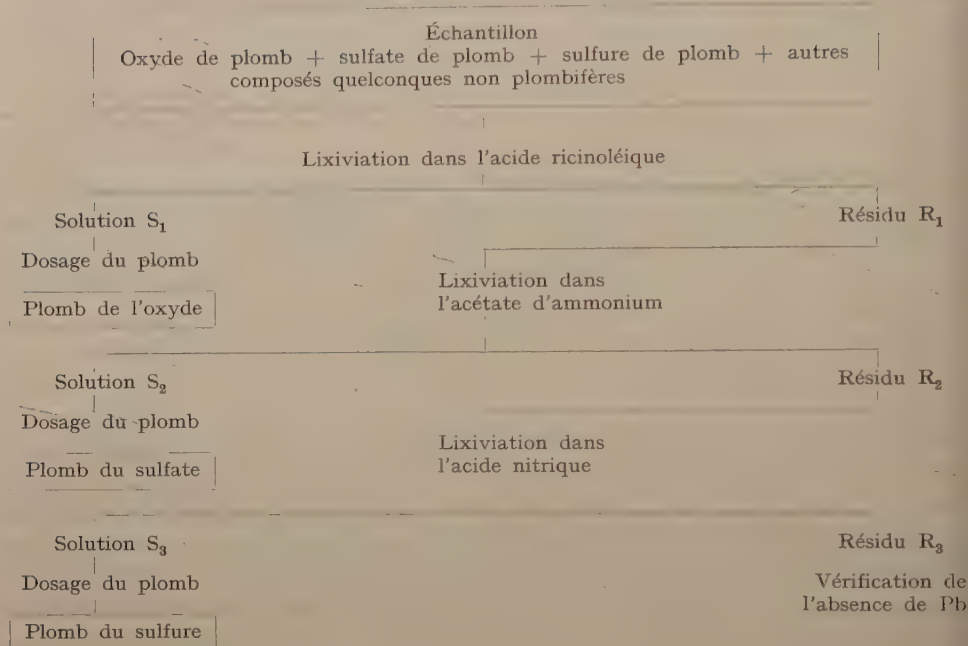
Lorsque les produits à analyser sont réputés particulièrement riches en composés plombifères, on peut éventuellement partir d'une prise d'essai de 2 g (au lieu de 5 g) dans le but de diminuer le nombre d'attaques.

La filtration sépare la solution S_1 du résidu R_1 .

Bibliographie p. 438.

TABLEAU I

SCHÉMA DE LA MÉTHODE



Analyse de vérification: dosage direct du plomb total dans l'échantillon initial

2. Détermination de l'oxyde de plomb

La solution S₁ est chauffée pour éliminer l'alcool. Celui-ci étant éliminé et le milieu étant limpide, ajouter une solution concentrée d'hydroxyde de sodium en excès puis faire passer l'acide sulfhydrique jusqu'à saturation et laisser décanter trois heures. Filtrer et vérifier l'absence du plomb dans le filtrat. Trouer le filtre et à l'aide d'un peu d'eau chaude (pissette), faire tomber la majeure partie du précipité dans un vase propre placé sous l'entonnoir. Reprendre alors le résidu restant sur le filtre par 150 ml d'acide nitrique à 50% avec addition de quelques gouttes de brome. Faire bouillir le tout jusqu'à réduction du volume liquide à environ 100 ml. Laisser refroidir jusqu'à moins de 30° C, ajouter 200 ml d'acide sulfurique 50% et évaporer jusqu'à fumées blanches. Reprendre par l'eau chaude (appliquer éventuellement le procédé de précipitation sélective du plomb exposé plus haut) et laisser reposer jusqu'à obtention d'un précipité bien décanté et bien grenu.

Le précipité de sulfate de plomb est filtré, lavé à l'eau chargée d'acide sulfurique (5 %), lavé à l'eau chaude puis à l'alcool éthylique (vérifier l'absence de plomb dans le filtrat). Le précipité est ensuite séché, calciné à 550° C pendant une heure et pesé. Le poids de plomb obtenu représente l'oxyde de plomb présent dans l'échantillon analysé.

Signalons ici que, au cours du lavage final du sulfate de plomb, l'alcool éthylique permet d'obtenir des résultats plus précis que ceux obtenus avec l'alcool méthylique.

3. Lixiviation dans l'acétate d'ammonium

Le résidu R₁ est attaqué par 250 ml d'une solution d'acétate d'ammonium à 50 %. La lixiviation se fait à chaud et l'ébullition est prolongée pendant une demi-heure. Le niveau du liquide est maintenu constant au moyen d'eau distillée dans le but de conserver la même concentration en acétate. Répéter éventuellement l'attaque jusqu'à dissolution complète du composé plombifère soluble (en général deux attaques suffisent). La filtration se fait à chaud et donne un résidu R₂ (lavé à l'eau chaude) et une solution S₂.

Bibliographie p. 438.

4. Détermination du sulfate de plomb

La solution S_2 est tout d'abord étendue par 300 ml d'eau chaude et portée à une température voisine de 80°C . Pendant ce temps, préparer une solution d'acide sulfurique à 20 % et chauffer cette solution également à 80°C (niveau constant). Verser lentement 100 ml de la solution sulfurique chaude dans la solution d'acétate. Laisser déposer le mélange à une température voisine de 40°C jusqu'à obtention d'un précipité bien décanté et bien grenu (2 à 3 heures). Filtrer la pulpe chaude, laver à l'eau sulfurique 5 %, à l'eau chaude, puis à l'alcool éthylique (vérifier l'absence de plomb dans le filtrat). Sécher le précipité, calciner une heure à 550°C et peser.

Le poids de plomb obtenu représente le sulfate de plomb présent dans l'échantillon analysé.

5. Détermination du sulfure de plomb

Le résidu R_2 est attaqué par 50 ml d'acide nitrique 50 % avec addition de quelques gouttes de brome. La solution est évaporée et reprise par de l'eau chaude. Laisser refroidir un peu, ajouter 100 ml d'acide sulfurique 50 %, et évaporer jusqu'à fumées blanches. Reprendre par l'eau chaude (appliquer éventuellement le procédé de séparation sélective du sulfate de plomb) et laisser déposer jusqu'à obtention d'un précipité bien décanté et bien grenu. Filtrer, laver à l'eau chaude sulfurique 5 %, à l'eau chaude et à l'alcool éthylique, sécher, calciner une heure à 550°C et peser. Le poids de plomb obtenu représente le sulfure de plomb présent dans l'échantillon.

La somme des teneurs en oxyde de plomb, en sulfate de plomb et en sulfure de plomb doit correspondre à la teneur de l'échantillon en plomb total.

F. CONCLUSIONS

La méthode proposée permet des séparations sélectives et constitue une amélioration du procédé préconisé par E. KROSSIN dans son article.

En effet,

- 1) Elle ne comporte aucun résultat établi par différence.
- 2) C'est une méthode continue d'opérations successives sur le même échantillon de départ.
- 3) Elle réduit le temps consacré à la préparation des échantillons (qui doivent être finement broyés) et augmente la précision de l'échantillonnage.
- 4) Elle utilise chaque produit des lixiviations jusqu'au résidu final où l'absence de plomb est vérifiée.
- 5) Elle assure le contrôle des résultats par des bilans exacts.

II. ÉTUDE DU SILICATE DE PLOMB, DU PEROXYDE DE PLOMB ET DU PLOMB MÉTALLIQUE

A. POSITION DU PROBLÈME

En ce qui concerne l'analyse des silicate, peroxyde et plomb métallique, nous n'avons trouvé aucune méthode susceptible d'orienter les recherches. Il a donc bien fallu se livrer à des investigations par tâtonnements sur l'action de plusieurs réactifs, et étudier plus en détail les réactifs donnant des résultats intéressants.

Il convient tout d'abord d'étudier l'action de l'acide ricinoléique et de l'acétate d'ammonium. Les essais montrent que le silicate est soluble tandis que le métal et le peroxyde sont insolubles. Le silicate accompagne donc l'oxyde au cours de l'analyse moléculaire.

B. ACTION DE L'ACIDE CHLORHYDRIQUE

Dans ces essais, l'échantillon est lixivié dans l'acide chlorhydrique. Le filtrat est traité par l'acide sulfurique 20%, et la gravimétrie du sulfate tandis que le résidu est redissous dans l'acide nitrique puis également traité par la gravimétrie du sulfate. Dans ces essais, nous avons fait varier la température de la lixiviation et la concentration de l'acide chlorhydrique. Des essais systématiques établissent que le peroxyde est complètement soluble dans l'acide chlorhydrique dilué froid tandis que le sulfure et le métal restent insolubles.

C. ACTION DU PERHYDROL

Les échantillons de sulfure et de plomb métallique sont lixiviés dans une solution de perhydrol. Après une filtration qui élimine l'excès d'eau oxygénée, le résidu est lavé et attaqué par une solution chaude d'acétate d'ammonium. Les filtrat et résidu de cette opération sont traités comme il est indiqué plus haut au cours de l'exposé relatif à l'action de l'acétate d'ammonium. Le perhydrol doit être rigoureusement exempt d'acides.

Les essais de dissolution ont montré qu'après ce double traitement le sulfure est complètement soluble tandis que le plomb métal est insoluble.

Le procédé présente néanmoins l'inconvénient de donner lieu à une réaction très violente au début de la lixiviation par le perhydrol. En conséquence nous avons modifié le mode opératoire en commençant les attaques par une solution diluée en perhydrol pour terminer par une lixiviation dans le perhydrol pur.

D. MÉTHODE D'ANALYSE MOLÉCULAIRE

En possession de ces données, nous avons complété la méthode donnée dans le Tableau I par celle représentée par le Tableau II.

Cette méthode s'est révélée très satisfaisante dans son application à des mélanges synthétiques obtenus en partant de produits réputés purs.

1. L'échantillon est tout d'abord traité par l'acide ricinoléique et l'acétate d'ammonium, comme il a été exposé en détail ci-dessus. On obtient de cette manière l'oxyde de plomb, le silicate de plomb, et le sulfate de plomb.

2. Le résidu R_2 résultant de l'attaque par l'acétate d'ammonium lixivié dans 500 ml d'une solution d'acide chlorhydrique avec agitation mécanique pendant deux heures (répéter éventuellement la lixiviation). La filtration sépare un résidu R_3 d'une solution S_3 . Celle-ci est évaporée puis traitée par l'acide sulfurique et la gravimétrie du sulfate comme nous l'avons déjà exposé. Le résultat du dosage correspond au peroxyde de plomb.

3. Le résidu R_3 est lixivié tout d'abord par 100 ml d'une solution de perhydrol à 10 % et ensuite par 100 ml de perhydrol pur. Après filtration, le produit est attaqué 30 minutes dans l'acétate d'ammonium chaud et le filtrat S_4 est traité par la gravimétrie du sulfate. On obtient ainsi le sulfure de plomb.

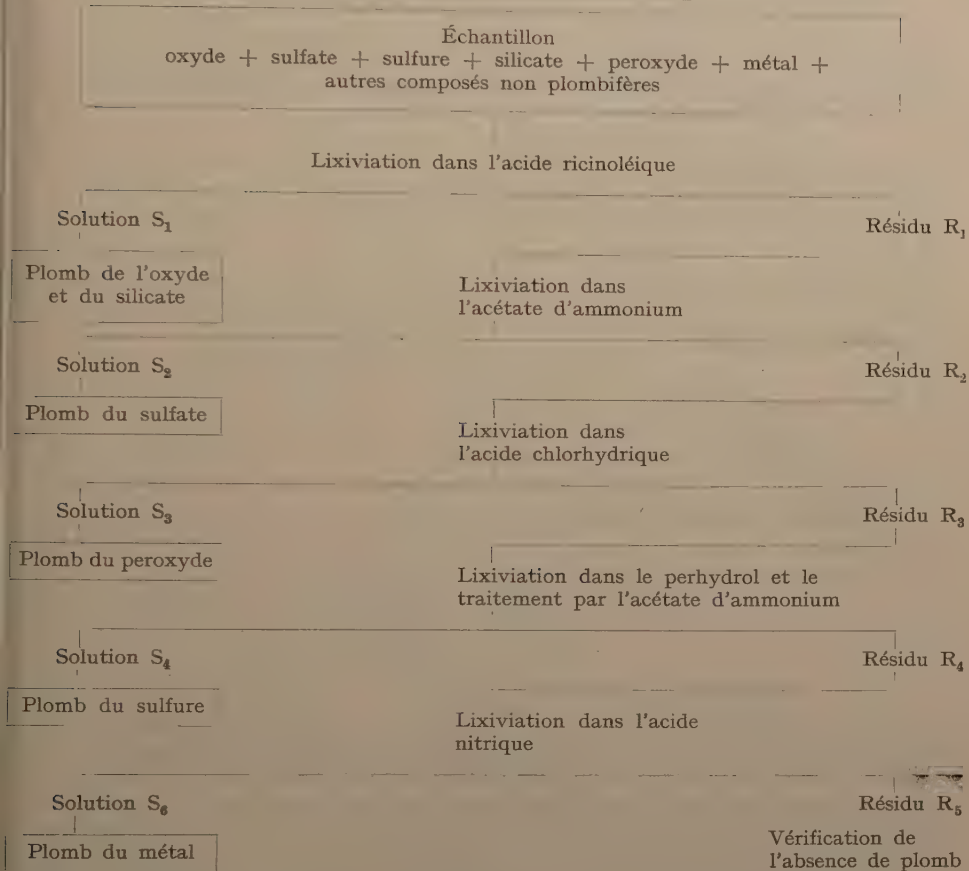
4. Le résidu R_4 subit le traitement à l'acide nitrique déjà décrit en détail dans la première partie de cette étude et le résultat représente le plomb métallique.

Il importe de vérifier l'absence de plomb dans le résidu final non attaqué par l'acide nitrique.

La méthode a été appliquée à des produits chauffés à diverses températures puis refroidis. Les résultats ont montré que la sélectivité des réactifs n'est pas affectée.

TABLEAU II

SCHÉMA DE PRINCIPE DE L'ANALYSE MOLÉCULAIRE



Analyse de vérification: dosage direct du plomb total dans l'échantillon initial.

tée et que seule est modifiée la durée de dissolution dans les réactifs. En particulier, l'attaque de l'oxyde dans l'acide ricinoléique est plus lente lorsque l'oxyde a été chauffé puis refroidi au préalable et devient encore plus paresseuse lorsque le chauffage a été suivi d'un refroidissement rapide.

L'analyse moléculaire a été également appliquée avec succès à des minerais de galène, des produits grillés et supergrillés et des mattes plombifères. La méthode préconisée est comparée aux anciennes déterminations dans le Tableau III en ce qui concerne le dosage chimique de l'oxyde, du peroxyde, du métal, du sulfure et du sulfate.

Telle qu'elle se présente, cette méthode d'analyse moléculaire peut faciliter de manière appréciable l'étude des problèmes métallurgiques relatifs aux minerais et aux produits métallurgiques plombifères. Elle permet notamment le contrôle automatique des analyses en proscrivant tout résultat obtenu par différence.

TABLEAU III

COMPARAISON ENTRE LES ANCIENNES DÉTERMINATIONS ET LA MÉTHODE PROPOSÉE

Anciennes déterminations	Méthode proposée
Détermination directe du Pb total (1)	Détermination directe du Pb total (1)
Détermination des composés non solubles dans l'acide ricinoléique. Par différence avec (1) on a l'oxyde de Pb (2)	
Détermination de la somme (oxyde + sul- fate) Par différence avec (2) on a le sulfate de Pb (3)	Déterminations directes et sélectives, sur une seule prise d'échantillon, de oxyde de Pb (2) sulfate de Pb (3) peroxyde de Pb (4) sulfure de Pb (5) Pb métallique (6)
Aucune détermination sélective du peroxyde de Pb (4) du sulfure de Pb (5) du Pb métallique (6) Seule la somme (4) + (5) + (6) peut être déterminée par différence entre (1) et (2) + (3)	
Aucun contrôle systématique des résultats obtenus	La somme (2 + 3 + 4 + 5 + 6) doit donner (1) Contrôle automatique des résultats

RÉSUMÉ

Cet article expose une méthode d'analyse quantitative de différents composés moléculaires du plomb présents dans des minerais et des produits métallurgiques. En principe, la méthode consiste à dissoudre sélectivement et successivement les différents composés plombifères et à doser le plomb dans chacune des solutions obtenues.

La méthode permet le contrôle automatique des analyses en proscrivant tout résultat obtenu par différence.

SUMMARY

This paper describes a method for the quantitative determination of various lead compounds present in ores and metallurgical products. The method consists, in principle, of dissolving selectively and successively the different lead compounds and determining the lead in each of the filtrates thus obtained.

The method guarantees the automatic control of the results.

ZUSAMMENFASSUNG

Dieser Artikel stellt eine quantitative Methode für die verschiedenen sich in Erzen und metallurgischen Produkten befindenden Bleiverbindungen dar. Das Prinzip der Methode besteht daraus dass die verschiedenen Bleiverbindungen selektiv und nach einander aufgelöst werden und das Blei in jedem erhaltenen Filtrat bestimmt wird.

Die Methode gestattet die automatische Kontrolle der Analysen, unter Vermeidung jedes durch Differenz erzeugten Resultates.

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A QUICK AND PRECISE HETEROMETRIC DETERMINATION OF IRON
WITH ALUMINON IN EXCESSES OF FOREIGN METALS

by

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INTRODUCTION

In a previous heterometric investigation the reaction of iron(III), chromium(III) and aluminium with aluminon was studied¹. The existence of a series of compounds was established and their character was investigated. It was shown that in mixtures containing all three cations the insoluble compounds of iron were heterometrically formed quantitatively, *before* any reaction with chromium or aluminium occurred. It was found that this was even the case in solutions which contained only a few tenths of one percent of iron. The working conditions and the influence of other foreign metals which were present in solution were studied. In all cases the titration of iron with aluminon proceeded smoothly and the titration lasted 10-15 minutes. In a 0.000375*M* solution of iron (= 0.2 mg Fe) containing more than 99.5% foreign metal, the determination could generally be made with an error of 0.2%. When the amount of iron analysed was as high as 0.5 mg, the error was always equal to zero. No previous separations whatever were necessary. The method presented is applicable in all cases where the thiocyanate method is impossible. The *end-point* of the titration is obtained at the molar ratio of 1 iron : 3 aluminon (= $\text{Fe}(\text{AN})_3 \downarrow$). It is very important that this point, derived from the curves, should be clear cut, should coincide with the *first* optical maximum density point and not change on further addition of titrant. It was ascertained that this was the case only with pure iron solutions. In the presence of other metals the maximum density values increased gradually and continuously with the further addition of titrant. Due to this the determination of the end-point became impossible. In contrast to the behaviour of other metals, *in the presence of chromium, a strictly horizontal line was obtained.*

It was found that the addition of a definite amount of a chromium salt was essential in all titrations in order to obtain a precise and safe *first* maximum optical density point. This addition of chromium was made when the iron was determined in excess of all other foreign metals tested.

EXPERIMENTAL

The same apparatus and the same technique were used as in previous heterometric investigations^{2,3}. All titrations were made using a thick and deep red filter (Corning No. 2408). The

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TABLE I

Composition: 9 ml aqueous solution + 1 ml M CH_3COOH + x ml mM aluminon (= AN).

Experiment number	Solution								Molarity of AN (=m)	% of iron
	$\text{Fe}(\text{NO}_3)_3$		$\text{Cr}(\text{NO}_3)_3$		Salt					
	ml	molar	ml	molar		name	ml	molar		
1	3	0.00125	—	—	—	—	—	0.00333		
2	3	0.00125	2	0.02	—	—	—	0.00333		
3	3	0.00125	2	0.1	—	—	—	0.00333		
4	3	0.00125	1	1.0	—	—	—	0.00333	0.4	
5	3	0.00125	2	1.0	—	—	—	0.00333	0.2	
6	3	0.00125	—	—	$\text{Al}(\text{NO}_3)_3$	1	0.1	0.00333	8	
7	3	0.00125	—	—	"	1	1.0	0.00333	0.8	
8	3	0.00125	—	—	"	1	3.0	0.00333	0.2	
9	3	0.00125	1	1.0	"	1	1.0	0.00333	0.4	
10	3	0.00125	1	1.0	$\text{Co}(\text{NO}_3)_2$	1	1.0	0.00333	0.3	
11	3	0.00125	1	1.0	$\text{Cu}(\text{NO}_3)_2$	1	1.0	0.00333	0.3	
12	3	0.00125	1	1.0	$\text{Ni}(\text{NO}_3)_2$	1	1.0	0.00333	0.3	
13	3	0.00125	1	1.0	$\text{Pb}(\text{NO}_3)_2$	1	1.0	0.00333	0.1	
14	3	0.00125	1	1.0	MnCl_2	1	1.0	0.00333	0.3	
15	4	0.00250	—	—	—	—	—	0.00666	—	
16	4	0.00250	2	1.0	—	—	—	0.00666	0.5	
17	4	0.00250	2	1.0	$\text{Al}(\text{NO}_3)_3$	2	1.0	0.00666	1.0	
18	4	0.00250	2	1.0	$\text{Co}(\text{NO}_3)_2$	2	1.0	0.00666	0.4	
19	4	0.00250	2	1.0	$\text{Ni}(\text{NO}_3)_2$	2	1.0	0.00666	0.4	
20	4	0.00250	2	1.0	$\text{Cu}(\text{NO}_3)_2$	2	1.0	0.00666	0.4	
21	4	0.00250	2	1.0	$\text{Pb}(\text{NO}_3)_2$	2	1.0	0.00666	0.1	
22	4	0.00250	2	1.0	$\text{Cd}(\text{NO}_3)_2$	2	1.0	0.00666	0.2	
23	4	0.00250	2	1.0	MnCl_2	2	1.0	0.00666	0.5	
24	4	0.00250	2	1.0	ZnCl_2	2	1.0	0.00666	0.4	
25	4	0.00250	2	1.0	MgSO_4	2	1.0	0.00666	1.1	
26	4	0.00250	2	1.0	$\text{Ba}(\text{NO}_3)_2$	2	1.0	0.00666	0.2	
27	4	0.00250	2	1.0	$\text{Ca}(\text{NO}_3)_2$	2	1.0	0.00666	0.7	

c = contact point.

chemicals used were all AnalaR or chemically pure reagents. The aluminon used was a British Drug House reagent. The iron nitrate solutions were prepared from a molar stock solution of iron containing nitric acid at a concentration of two molar. The iron solution was diluted in steps in order to give the desired final molarity. Although the obtained dilute solutions contained free nitric acid they were freshly prepared for each series of titrations. In all titrations the analysed volume was made with water to equal 10 ml. A microburet of 5 ml volume (0.01 ml) was used, the reaction vessel was cylindrical and had a diameter of 4 cm. The temperature of the vessel was thermostatically controlled at 20°C. The aluminon was dissolved in water. Generally, the end-point of the titration was obtained from enlarged heterometric titration curves, by the intersection of two lines, the maximum density line and the line of the last quarter of the titration curve.

RESULTS AND DISCUSSION

General

Table I and Figs. 1-3 contain a small selection of the titrations made. The numbers are the same in the table and in the curves. The composition of each experiment may be read from the table. In the table the calculated percentage of iron in the mixture was made on the basis of the sum of the iron and foreign metals present, but the added chromium was not taken into account. Only when chromium was considered the foreign metal was the % of iron calculated in relation to the chromium.

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Content iron: 0.2097 mg or 0.5592 mg. T = 20° C. Red filter Corning (No. 2408)

x ml AN calculated at:		x ml AN found at:		Optical density at:		% error at:	Titration time in minutes	Remarks
1:3		1:1		1:1		1:3		
13	3.38	1.0	3.46	0.31	0.42	+2.4	15	
		—	3.40	0.31	0.40	+0.6	15	Horizontal maximum line
		—	3.40	0.30	0.41	+0.6	10	" " "
		—	3.40	0.18	0.34	+0.6	12	" " "
		—	3.42	—	0.25	+1.2	15	Slightly increasing maximum line
		—	—	—	—	—	—	A continuously increasing
		—	—	—	—	—	—	optical density line without
		—	—	—	—	—	—	breaks.
		—	3.40	—	0.29	+0.6	15	Horizontal maximum line
		—	3.50	—	0.37	+3.6	10	" " "
		—	3.45	—	0.32	+2.1	10	" " "
		—	3.46	—	0.36	+2.3	10	" " "
		—	3.45	—	0.33	+2.1	10	" " "
		—	3.45	—	0.31	+2.1	10	" " "
50	4.50 c	1.6	4.50	0.72	0.99	0.0	10	" " "
		—	4.50	—	0.62	0.0	10	" " "
		—	4.50	—	0.57	0.0	15	" " "
		—	4.50	—	0.64	0.0	15	" " "
		c 1.6 c	4.50	—	0.48	0.0	15	" " "
		—	4.50	—	0.36	0.0	10	" " "
		—	4.50	—	0.67	0.0	10	" " "
		—	4.50	—	0.69	0.0	10	" " "
		—	4.50	—	0.69	0.0	10	" " "
		—	4.50	—	0.73	0.0	10	" " "
		—	4.50	—	0.67	0.0	10	" " "
		—	4.50	—	0.73	0.0	10	" " "
		—	4.50	—	0.67	0.0	10	" " "
		—	4.50	—	0.73	0.0	10	" " "
		—	4.50	—	0.67	0.0	10	" " "

In all cases (with the exception of expts. 6-8) *horizontal* maximum density lines were obtained at the end of the titration.

Many titrations of iron were carried out in the presence of excesses of bivalent cations; but in the absence of chromium, in no case was a horizontal maximum line obtained. The density values continued to increase after the calculated end-point had been reached. As to the amount of chromium nitrate which was added the following may be said: the maximum amount of foreign metal which was safely present in the iron solution without causing difficulty in the location of the end-point depended on the amount of chromium added. It was ascertained that the chromium must be present in a molar ratio of at least *one* chromium to *one* metal. Small quantities of iron, even in the absence of foreign metals, gave a heterometric curve with a slightly rising maximum density line. In this case, too, the addition of chromium was helpful, the maximum density line being strictly horizontal. On the other hand, the addition of large excesses of chromium decreases the maximum density value and impedes the determination.

As to the additional critical point obtained at the molar ratio of *one* iron to *one* aluminon (see previous report), this point almost disappeared in the presence of

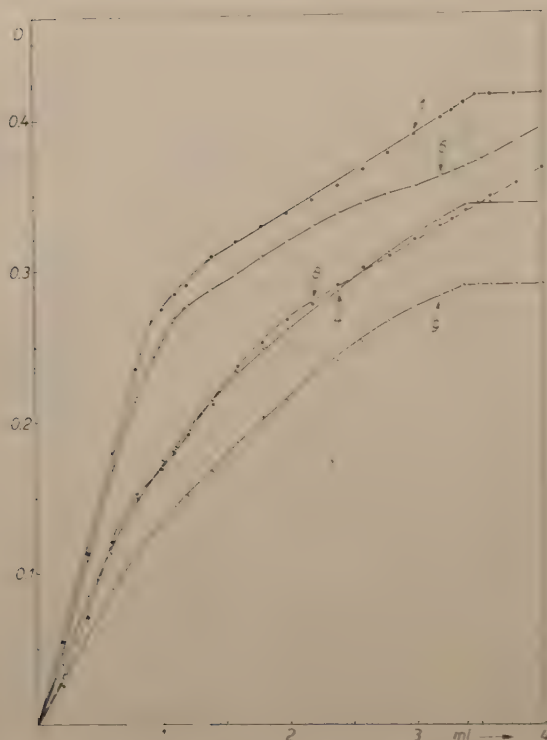


Fig. 1. Titrations of iron with aluminon in excesses of chromium and aluminium.

chromium. In specific cases it could be located from the curves by extrapolation, but the location was very uncertain.

Titrations in the presence of trivalent cations

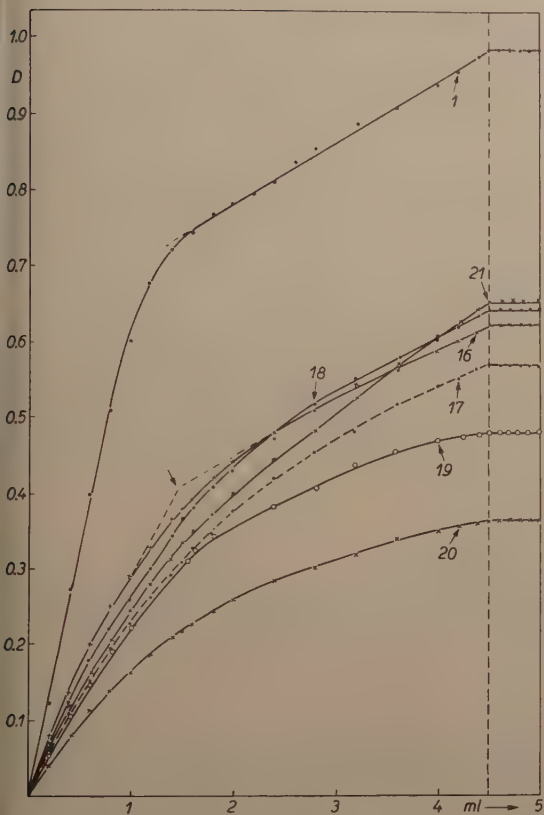
Table 1 and Figs. 1 and 2 give results with aluminium and chromium.

In the presence of aluminium alone (without chromium) the curves showed no end-point for iron, even when the latter was present in large amounts (Table 1, expts. 6-8 and Fig. 1). The addition of chromium nitrate makes the determination easy and safe. The solution could contain 99.5% aluminium, the error was 0.6% or zero (expts. 9 and 7). The maximum density values obtained decreased somewhat in comparison with the blanks (expts. 1 and 15), therefore the use of a higher amount of iron for the analysis is preferable (expt. 17).

In the presence of chromium. The content of chromium could be 99.5%. The titration time was 10 minutes and the error was zero (expt. 16). The maximum density value is reduced by one third.

Titrations in the presence of bivalent cations

The iron could be analysed in the presence of 99.5% of the following foreign metals: Pb, Cd, Cu, Co, Ni, Mn, Zn, Mg, Ba, Ca. To all solutions analysed, an amount of chromium nitrate must be added, which is equal or exceeds mole to mole the amount of the sum of the foreign bivalent cations. An excess of chromium caused no harm to the precision of the determination; 0.2-0.5 mg iron had to be used for the analysis.



With the higher amounts of iron the determination could be carried out with an error equal to zero.

On the specific action of chromium

It can be seen from the material presented that iron can be analysed in the presence of foreign metals *only after the addition of chromium nitrate*. The question arises, what is the specific action of chromium and how can that action be interpreted?

From previous work on aluminon it is known that chromium forms insoluble complex compounds with aluminon which are probably next in stability to the compounds similar to iron. The chromium complexes are therefore probably formed (in the presence of excesses of foreign metals) with the excess of

Fig. 2. Titration of iron with aluminon in excesses of trivalent and bivalent salts.

aluminon *after* the quantitative precipitation of $\text{Fe}(\text{AN})_3$ has occurred. There is a large excess of chromium in solution and the compound which is formed under all conditions must therefore have the composition of $\text{Cr}_1(\text{AN})_1$. This last, however, remains *dissolved* under the working conditions described here. The excess of aluminon is therefore used up in forming the soluble chromium compound and a *horizontal* maximum density line is obtained.

Similar effects were obtained with trivalent phthalates⁴. At the same

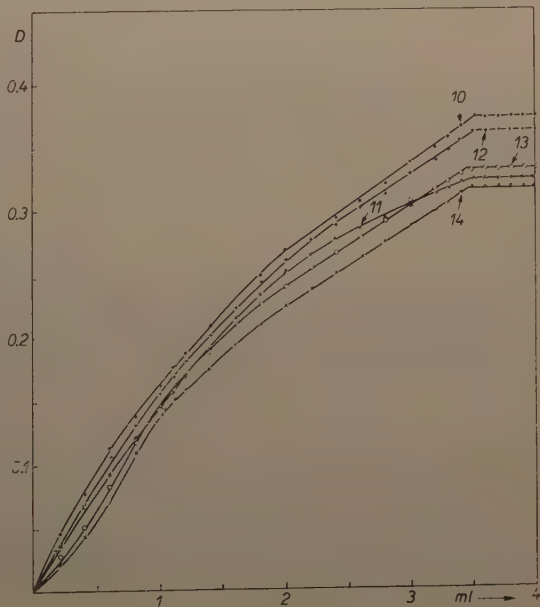


Fig. 3. Titrations of iron with aluminon in excesses of bivalent salts.

composition and concentration of the complexes we obtained either an insoluble or a soluble compound, and this depended on the working conditions.

On the other hand, when a dilute solution of an iron salt was titrated with aluminon even in the absence of foreign metals, the excess of aluminon itself somewhat increased the density after the maximum point had been reached and a line of increasing density may be obtained. Due to the presence of a chromium salt the added aluminon is bound to the chromium and we obtain a safe *horizontal* maximum density line.

PROCEDURE

The solution of ferric iron which has to be analysed must be acidified with nitric acid. The molarity of nitric acid must be equal or double the molarity of the iron. The solution is then diluted to give an iron concentration equal to 0.0004M-0.001M (or 0.2-0.5 mg Fe). The analysed solution may contain, in addition to iron, other tri- or bivalent metals which may make up $\leq 99.5\%$ of the total metal content.

METHOD

1. Analysis in the absence of excesses of foreign metals

Ten ml of an aqueous solution of an iron salt, which contain 0.2-0.5 mg ferric iron and in addition 1 ml M acetic acid are titrated heterometrically with a 0.003-0.006M aqueous solution of aluminon. It is advisable to add 1 ml 0.1M $\text{Cr}(\text{NO}_3)_3$ to the analysed solution.

Titration time: 10-15 minutes.

Error: zero to 2%.

2. Analysis in the presence of large excesses of foreign metals

Ten ml of an aqueous solution of iron salt which contain 0.2-0.5 mg ferric iron and in addition 1 ml M acetic acid and 1 to 2 ml M $\text{Cr}(\text{NO}_3)_3$ are titrated heterometrically with 0.003-0.006M solution of aluminon.

Titration time: 10-15 minutes.

Error: zero to 2%

SUMMARY

A method is presented for the heterometric determination of 0.2-0.5 mg ferric iron with aluminon. The analysed solution may contain excesses of coloured or colourless foreign bi- or trivalent cations. The latter may make up $\leq 99.5\%$ of the total metal content. The working conditions were studied. The determination lasts 10-15 minutes and the error is 0-2%.

RÉSUMÉ

Une méthode est proposée pour le dosage hétérométrique du fer(III) (0.2-0.5 mg) au moyen d'aluminon. La solution à analyser peut renfermer un excès de cations bi- ou trivalents colorés ou incolores; ces derniers peuvent représenter jusqu'à 99.5% du total. Les conditions de travail ont été étudiées. Le dosage s'effectue en 10-15 minutes. L'erreur est de 0 à 2%.

ZUSAMMENFASSUNG

Eine Methode zur heterometrischen Bestimmung von 0.2-0.5 mg Eisen(III) mit Aluminon wird vorgelegt. Die zu analysierende Lösung kann Überschüsse von gefärbten oder farblosen zwei- oder dreiwertigen Kationen enthalten. Letztere können $\leq 99.5\%$ vom Gesamtgehalt ausmachen. Die Arbeitsbedingungen wurden studiert. Die Bestimmung dauert 10-15 Minuten und der Fehler ist 0-2%.

References p. 445.

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COLORIMETRIC DETERMINATION OF OSMIUM(VI) WITH 1-NAPHTHYLAMINE-3,5,7-TRISULFONIC ACID

by

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INTRODUCTION

The importance of osmium in the fields of metallurgy^{3,4,6}, biology³, medicinal chemistry¹, and possibly chemotherapy⁷ justify search for a colorimetric method which is both simple and precise for its quantitative determination. Although a number of reactions have been proposed for the determination of osmium, the ones that have been developed leave much to be desired. Of the colorimetric reagents now available, thiourea is by far the best suited for analytical application and has been the one most commonly used.

We have developed a new colorimetric method based on the stable violet complex formed by the reaction of osmium (OsO_4^{-2}) with 1-naphthylamine-3,5,7-trisulfonic acid. Further work must be carried out to determine whether or not the method herein proposed is of general use, because it requires that the osmium be in the VI valence state and this limits the application of the reagent. Our investigation shows, however, that the reagent is useful for the identification of hexavalent osmium and for its quantitative determination in trace quantities. Compared with colorimetric methods described in the literature the new method has a higher sensitivity (1 part of osmium in 15,000,000 parts of solution). Other advantages are simplicity of operation and the fact that the reaction is carried out in weakly acidic medium (adjusted to pH 1.5) in contrast to a strongly acid one required for the thiourea method, for example. The chief disadvantage is the limitation of the color reaction to VI valent osmium.

APPARATUS

All absorbance measurements were made with a Beckman spectrophotometer, Model DU, using matched 1.00 cm Corex cells. At wavelengths of 625 $\text{m}\mu$ or below, the ultraviolet-sensitive phototube was used; above 625 $\text{m}\mu$, the red-sensitive phototube. The phototube circuit was kept at maximum sensitivity and under these conditions the slit width at 560 $\text{m}\mu$ was about 0.04 $\text{m}\mu$, corresponding to a nominal band width of 2.3 $\text{m}\mu$.

A Beckman pH meter, Model G, was used for all pH measurements. The meter was calibrated from time to time, using Leeds and Northrup standard buffer of pH 4.

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REAGENTS

Standard osmium solution. A standard solution containing 100 p.p.m. osmium was prepared by dissolving 0.0196 g of potassium osmate ($K_2OsO_4 \cdot 2H_2O$), obtained from American Platinum Works, in distilled water and diluting to the mark in a 100 ml volumetric flask. According to FRIEND², this solution is quite stable, though we observed some evidence of decomposition, a small black deposit appearing at the top of the volumetric flask after about one week. At higher temperatures, about 31° C, the solution is much less stable, the osmate decomposing into the volatile osmium tetroxide and osmium dioxide or metallic osmium. For best results the solution should be kept between 15° and 25° C. Over this temperature range no decomposition was noted.

Reagent solution. $5.3 \cdot 10^{-4}M$. Dissolve 0.0505 g of 1-naphthylamine-3,5,7-trisulfonic acid in water, dilute to 250 ml and mix. The compound may be obtained from the LaMotte Chemical Products Co., Towson, Baltimore, Md. (U.S.A.).

Buffer solutions. Buffer solutions were the Clark and Lubs type, prepared by mixing 97 ml of 0.2N hydrochloric acid and 50 ml of 0.2N potassium chloride and diluting to 200 ml.

Other reagents. All other reagents were of analytical grade and were used without further purification.

EXPERIMENTAL

Absorbance curves. An absorbance curve of the reagent solution ($5.3 \cdot 10^{-4}M$) is shown in Fig. 1. The reagent absorbs only in the low wavelength portion of the visible region and at the maximum for the organo-osmium complex its absorbance is negligible. Hence excess reagent does not appreciably increase the absorbance reading of the solution. Experiments showed that the amount of excess is not important provided a 7 : 1 ratio is not exceeded.

Fig. 1 also shows an absorbance curve for the organo-osmium complex. The complex was formed by adding excess reagent to 4 p.p.m. osmium as OsO_4^{-2} . The curve shows a sharp peak at 560 $m\mu$.

Effect of pH. The organo-osmium complex shows wide variation with change in pH, having maximum absorbance at pH 1.5. The purple color first formed upon addition of the reagent to a solution of osmium(VI) changes to violet at pH 1, to blue at higher pH values and finally to a pale green at pH 10 to 11.

Rate of reaction and stability of the complex. The formation of the organo-osmium complex was found to be dependent upon the reaction time. The color intensity increased up to four hours, after which the absorbance remained nearly constant. Absorbance readings of the colored complex taken over a period of one month showed no significant change; a stability quite adequate for analytical applications.

Beer's law. The organo-osmium complex adheres to Beer's law over an osmium concentration of 0 to 6 p.p.m., with a practical range of 1.5 to 5.5 p.p.m., corresponding to absorbance readings of 0.2 to 0.7 unit.

Sensitivity. According to SANDELL's expression of sensitivity⁹ and using an absorbance value of 0.119 for 1 p.p.m. osmium, the sensitivity is 0.01 γ per sq cm. However, for general use, the practical sensitivity is 0.067 γ per sq cm, i.e., 1 part of osmium in 15,000,000 parts of solution. Six solutions containing this concentration of osmium gave absorbance readings of 0.009, 0.010, 0.012, 0.011, 0.005, and 0.010 unit, respectively.

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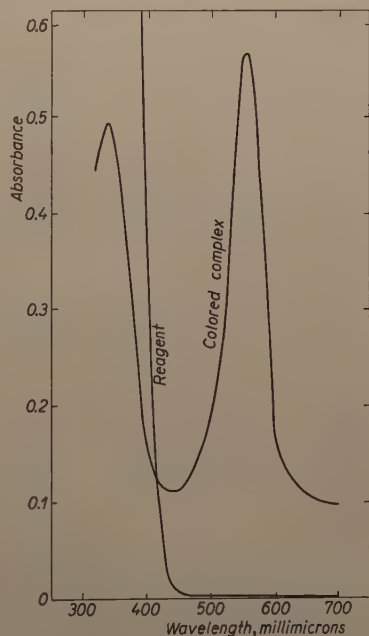


Fig. 1. Absorbance curves for 1-naphthylamine-3,5,7-trisulfonic acid and for its osmium(VI) complex, respectively.

Effect of temperature and order of adding solutions. Allowing maximum color intensity of the complex to develop over a temperature range of 15° to 35° C, the absorbance of the complex developed at 35° C was a little higher than at 15° C, but not enough to warrant raising the temperature above room temperature for color development.

Time for maximum color development of the complex must be allowed before the buffer is added to adjust the pH to 1.5; failure to do so results in decrease in absorbance.

Diverse ions. To determine interference by diverse ions, solutions were prepared containing 4 p.p.m. osmium, reagent, and varying concentrations of each ion to be tested. An increase or decrease of 0.005 unit in absorbance was taken as an interference. The following ions in concentration greater than 1:1, were found to cause an interference: Ru^{+3} , Rh^{+3} , Pd^{+2} , Ir^{+4} , Pt^{+4} , Al^{+3} , VO^{+} , Cr^{+3} , Fe^{+3} , Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Pb^{+2} , Mn^{+2} , Mg^{+2} , and Ag^{+} . These results indicate that osmium must be separated from many of the metallic ions before it can be determined by this method.

Results of analysis. Ten solutions containing 4 p.p.m. osmium as OsO_4^{-2} were treated according to the proposed procedure and their absorbance measured at 560 $\mu\mu$. The average absorbance was 0.564 unit, with an average deviation of 0.001, *i.e.* a relative deviation of about 0.2%, a precision which is quite good.

Osmium complex in solution. Three methods were employed to establish the empirical formula of the complex *in solution*. These were the mole ratio method of YOE AND JONES¹³, the continuous variations method of JOB⁸ with modification by VOSBURGH AND COOPER¹² and the slope ratio method proposed by HARVEY AND MANNING⁵. Results of the three methods indicate a complex formed by two molecules of reagent reacting with one osmate ion. The several irregular points on the curves are probably due to the fact that when excess osmium(VI) is present in acid solution it tends to reduce to colloidal oxides or metallic osmium.

In the YOE AND JONES method a series of solutions is prepared containing a constant amount of metallic ion but with increasing ratios of reagent to metal (or *vice versa*). The absorbances of the solutions are measured and plotted against the concentration ratios. The resulting curve should be a straight line rising until the combining ratio of reagent to metal ion is reached, after which it should break abruptly.

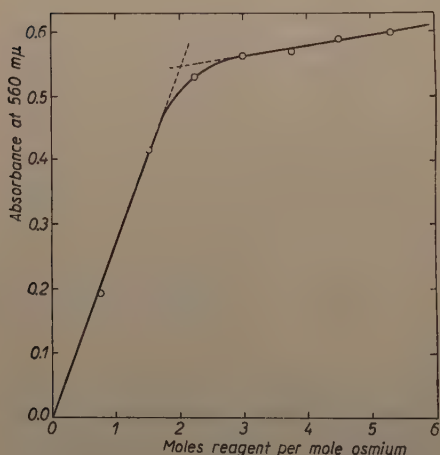


Fig. 2. Ratio of reagent to osmium by the "mole ratio" method.

Applying this method to the organo-osmium complex, solutions were made in which the osmium concentration was kept constant at $5.3 \cdot 10^{-4}M$ and the ratio of moles of reagent to moles of osmium varied from 0.7 to 5.2. A water blank was used for all absorbance measurements at 560 $\mu\mu$. In Fig. 2 the results show a 2 to 1 ratio of reagent to osmium.

JOB's method of continuous variations involves the preparation of a series of solutions in which the mole per cent of two substances forming a compound is varied and a physical property of the solution is measured. The physical property measured in this investigation is the absorbance of light at a given wavelength. A plot of the difference between the observed value and the value calculated assuming no reaction,

should show a maximum or a minimum at the mole percent corresponding to the compound formed.

In applying this method to the organo-osmium complex, solutions were prepared containing X ml, of a $5.3 \cdot 10^{-4}M$ reagent solution and $6-X$ ml of a $5.3 \cdot 10^{-4}M$ osmium solution. After standing four hours, buffer was added, the solution diluted to 25 ml with distilled water and mixed. Absorbances of the solutions were then measured at $560 \text{ m}\mu$. If the formation of the osmium complex is represented as follows, where n may be any number and R indicates reagent,



and the function Y is such that

$$Y = A_s(\text{obs.}) - A_s(\text{calc.}),$$

then a plot of the function Y against X should show a maximum (or minimum) at a point where

$$\frac{X}{6-X} = n.$$

Results as shown in Fig. 3, indicate a reagent to osmium ratio of 2 to 1. Here $X = 4$, hence $n = 2$.

The slope ratio method of HARVEY AND MANNING employs two sets of solutions. In the first set, the concentration of one of the reactants is maintained constant and in excess, while the concentration of the other is varied. In making the second set, the same procedure is followed but the moles of the two reactants are reversed. The absorbance of each solution is measured and plotted against concentration of the variable reactant.

The slope ratio method was applied to the organo-osmium complex as follows: One series of solutions was prepared containing 20 p.p.m. of osmium (an excess), buffer, and varying concentrations of reagent. Absorbance readings of the solutions were measured against a water blank at $560 \text{ m}\mu$. Another series of solutions were prepared in which the reagent concentration was constant and in excess, buffer was added and the amounts of osmium varied. Absorbances were measured against a reagent blank. Results are shown in Fig. 4. The ratio of the two slopes should be equal to the ratio of reagent to metal:

$$\frac{\text{Slope 2}}{\text{Slope 1}} = \frac{\text{reagent}}{\text{osmium}}$$

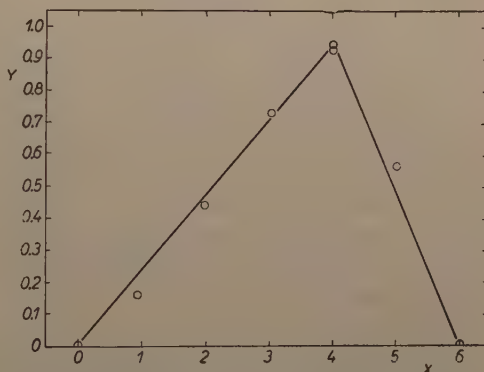


Fig. 3. Ratio of reagent to osmium by the "continuous variations" method.

From the data of Fig. 4, slope 2 = 0.1082 (reagent in excess) and slope 1 = 0.0560 (osmium in excess) and the reagent to osmium ratio is therefore

$$\frac{0.1082}{0.0560} = 1.93 \text{ — i.e., a ratio of 2 to 1 (within the limits of error).}$$

The results of the three methods indicate that *in solution* the ratio of reagent to osmium is 2 to 1. Solutions of 1-naphthylamine-6-sulfonic acid and 1-naphthyl-

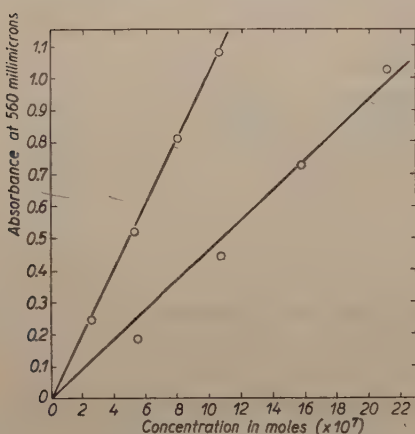


Fig. 4. Ratio of reagent to osmium by the "slope ratio" method.

amine each give the characteristic purple color with osmium(VI), the latter precipitating after standing about a half hour. This indicates that the colored compound produced by osmium(VI) and 1-naphthylamine-3,5,7-trisulfonic acid is the result of a reaction at the amino group.

Attempts at quantitative separation and determination of osmium in the hexavalent state. Two methods have been employed for the quantitative separation of osmium from all other elements. These are distillation^{3,11} and extraction with chloroform¹⁰. Both methods separate osmium in the octavalent state. Since the determination with 1-naphthylamine-3,5,7-trisulfonic acid requires that the osmium be present in its hexavalent

state, the problem is to reduce the osmium quantitatively from the octavalent to the hexavalent state. Attempts to do this met with no success. Whenever reducing agents were first applied to the osmium(VIII) solutions and then reagent added, the colors obtained were light red or orange instead of violet. In some cases no color developed at all.

The general use of 1-naphthylamine-3,5,7-trisulfonic acid as a reagent for osmium is dependent upon success in obtaining a quantitative reduction of osmium to the hexavalent state after its separation from other elements. If a suitable reducing agent can be found, it should be possible to apply the proposed colorimetric method to determine osmium in any material after its isolation either by distillation or extraction. Work along these lines is being continued.

SUMMARY

An investigation has been made of the organic compound, 1-naphthylamine-3,5,7-trisulfonic acid, for use as a colorimetric reagent for the determination of trace quantities of osmium(VI). When this compound is added to an osmium (OsO_4^{2-}) solution, a violet colored organo-osmium complex is formed which has highest sensitivity at wavelength 560 μ . The complex reaches maximum color intensity after four hours. The solution should be brought to pH 1.5 and maintained at this pH with a buffer, after maximum color development. The colored complex conforms to Beer's law over an osmium concentration range of 0 to 6 p.p.m. Its absorbance is not affected by either excess reagent (up to a 7 : 1 ratio) or by temperature variation over the range 15° to 35° C. Many metallic ions interfere with the color reaction and hence require a separation of osmium from these ions.

The nature of the complex *in solution* was studied by the following three methods: (1) mole ratio, (2) continuous variations and (3) slope ratio. All three methods indicate a ratio of reagent to osmium of 2 to 1.

A procedure for the colorimetric determination of osmium(VI) has been developed; it has a sensitivity of 1 part osmium in 15,000,000 parts of solution, with good precision.

RÉSUMÉ

Une étude a été effectuée sur l'acide 1-naphtylamine-3,5,7-trisulfonique, comme réactif colorimétrique pour le dosage de traces d'osmium (VI). Ce réactif donne avec l'osmium (OsO_4^{-2}) un complexe de coloration violette qui présente le maximum de sensibilité à la longueur d'onde de 560 m μ . La coloration du complexe formé atteint son maximum d'intensité après quatre heures. La solution doit être portée au pH 1.5 et maintenue à ce pH à l'aide d'un tampon, après le développement maximum de la coloration. La coloration obtenue suit la loi de Beer pour des concentrations d'osmium allant de 0 à 6 p.p.m. L'absorption n'est pas gênée par un excès de réactif (jusqu'à un rapport 7 : 1) ou par une variation de température de 15 à 35° C. Plusieurs ions métalliques gênent, ce qui nécessite une séparation de l'osmium. La nature du complexe *en solution* a été étudiée par trois méthodes différentes. Toutes ces méthodes indiquent un rapport réactif/osmium de 2/1. Un procédé de dosage colorimétrique de l'osmium(VI) est proposé; on arrive à une sensibilité de 1 partie d'osmium pour 15,000,000 parties de solution, avec une bonne précision.

ZUSAMMENFASSUNG

Es wurde eine Untersuchung ausgeführt über die 1-Naphtylamin-3,5,7-trisulfonsäure, als kolorimetrisches Reagenz für die Bestimmung von Spuren von Osmium(VI). Dieses Reagenz gibt mit dem Osmium (OsO_4^{-2}) einen violetten Komplex, welcher die grösste Empfindlichkeit bei der Wellenlänge 560 m μ aufweist. Die Färbung dieses Komplexes erreicht ihre maximale Intensität nach vier Stunden. Die Lösung muss auf pH 1.5 gebracht und mit Hilfe einer Pufferlösung auf diesem pH gehalten werden nachdem die stärkste Farbintensität erreicht ist. Die Färbung folgt dem Beerschen Gesetz für Konzentrationen von Osmium von 0-6 p.p.m. Die Absorption wird durch einen Überschuss an Reagenz (bis zu einem Verhältnis von 7 : 1) oder durch Temperaturschwankungen zwischen 15-35° nicht gestört. Mehrere Metallionen stören, was die Abtrennung des Osmiums verlangt. Die Art des Komplexes in Lösung wurde mit Hilfe von drei verschiedenen Methoden untersucht. Alle diese Methoden geben ein Verhältnis Reagenz/Osmium, 2/1. Es wird ein Verfahren zur kolorimetrischen Bestimmung von Osmium(VI) vorgeschlagen. Man erreicht eine Empfindlichkeit von 1 Teil Osmium in 15,000,000 Teilen Lösung, mit einer guten Präzision.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF FLUORIDE V. THE USE OF THE ALUMINIUM-CHROMEAZUROL-S COMPLEX

by

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In the previous paper¹ in the present series the aluminium chromeazurol S complex was suggested as a sensitive reagent for the determination of fluoride; it was not however expected to be as sensitive as the aluminium-eriochromecyanin complex, and the latter reagent was tested first. As difficulties were encountered during the development of the method using the aluminium-eriochromecyanin complex it was decided to try out the present method and the development of the two methods was completed simultaneously. In practice the chromeazurol S method has proved more sensitive than expected and in some ways has advantages over the one using eriochromecyanin although for ultimate sensitivity the latter is preferred.

EXPERIMENTAL

The previous work on haematoxylin^{2,3} and eriochromecyanin¹ had indicated that when using an aluminium-dye system as reagent for the determination of fluoride the best results were obtained at pH values of 4.0-4.7 and preliminary experiments showed that with the present system the most satisfactory complex was obtained at a pH of 4.25. The complex tends to precipitate on standing but addition of gum arabic produces a satisfactory stock solution of complex which is stable over a period of several weeks. The complex has a comparatively sharp peak at 5500 Å.

The effect of a change in ionic strength of solutions used was found to be similar to that experienced in the case of the eriochromecyanin complex and was again overcome by increasing the ionic strength of the solutions sufficiently to swamp minor variations; this was done as before by making the stock 0.5M and the buffer 2M with respect to ammonium chloride.

REVINSON AND HARLEY⁴ used the thorium salt of chromeazurol S in a similar manner to determine fluoride. We have tried their method and in general confirm their findings. The thorium complex behaves much as expected.

METHOD

A. Reagents

(i) Standard fluoride solution

Dissolve 0.5525 g of sodium fluoride in water and dilute to 250 ml. Dilute 1 ml of this solution to 100 ml.

1 ml = 10 µg F.

The purest available material should be used; that supplied by BAKER AND ADAMSON to A.C.S. specification is suitable.

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(ii) *Standard aluminium solution*

Dissolve 1.867 g "AnalaR" quality aluminium ammonium sulphate ($\text{Al}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in water and dilute to 100 ml.

1 ml = 1.11 mg Al.

For use dilute 10 ml of the above solution to 100 ml.

1 ml = 111 μg Al.

(iii) *Chromezurol S solution 0.275%*

Dissolve 0.275 g of solid in 10 ml of 0.1M hydrochloric acid and dilute to 100 ml.

(iv) *Ammonium hydroxide 9M*(v) *Glacial acetic acid*(vi) *Gum arabic 5%*

Dissolve 5 g of finely crushed solid in approximately 80 ml of freshly boiled water at 70° C (ca.). Filter while still hot through glass wool and dilute to 100 ml with freshly boiled water.

(vii) *Buffer solution (pH 4.25)*

Dissolve 32 g "AnalaR" quality ammonium chloride in 200 ml of water. Add 40 ml glacial acetic acid and 10 ml concentrated ammonia (sp.gr. 0.88). Cool to room temperature and adjust pH to 4.25 by further addition of ammonia using a pH meter. Dilute to 300 ml, check pH and again adjust to 4.25 if necessary.

B. *Procedure*(a) *Preliminary treatment*

Separate the fluoride from interfering ions, if necessary, by distillation from sulphuric acid in the presence of silica according to the method of WILLARD AND WINTER⁵. Collect 160 ml of distillate. If a micro-apparatus such as that described by HORTON THOMASON AND MILLER⁶ or by MACNULTY AND BARRETT⁷ is used only 10-20 ml need collected. Treat distillate as described below.

(b) *Treatment of distillates*(I) *For distillates of acid content equivalent to less than 1 ml of 1M acid per 150 ml*

This applies also to samples where distillation is not necessary, e.g. water.

(i) Neutralize the distillate to phenolphthalein with 0.1M sodium hydroxide.

Record the volume of the neutralized solution and the volume of alkali used.

(ii) Prepare a blank solution by neutralizing a volume of 0.1M sodium hydroxide equal to that used in step (1) with 0.05M sulphuric acid using phenolphthalein as indicator. Dilute the solution to a volume equal to that of the neutralized distillate.

(II) *For distillates of high acid content*

(i) Add sufficient 9M ammonium hydroxide to the distillate to bring the pH to 7 and note the volume required. Add 1 ml of glacial acetic acid and adjust the pH to 4.25 by further addition of ammonium hydroxide and again note the volume used.

(ii) Prepare a blank solution by adding 1 ml of glacial acetic acid to a volume of 9M ammonium hydroxide equal to the total amount used in step (1). Add acid (of the kind present in the distillate) to bring the pH to 4.25. Dilute the solution to a volume equal to that of the neutralized distillate.

(c) *Determination of fluoride*

(i) Place a suitable volume of the neutralized distillate in a 50 ml flask and an equal volume of blank solution in a second 50 ml flask. Add 2 ml of buffer solution to each flask and mix well.

(ii) Into each flask pipette 15 ml aluminium-chromezurol stock solution (see paragraph C.). Make up to the mark with water and mix well.

(iii) Place flasks in a water bath at 60° for 15 minutes. Cool to room temperature by immersion in a cold water bath.

(iv) Measure the difference between the absorbancies of the two solutions using a Hilger-Spekker absorptiometer with yellow green 605 filters and 2 cm cells, or a similar suitable instrument.

(v) Calculate the fluoride present by reference to a prepared calibration graph.

C. *Preparation of aluminium-chromeazurol stock solution*

To 425 ml of water in a 600 ml beaker add in order the following mixing well after each addition.

- (i) 13.4 g ammonium chloride
- (ii) 3 ml glacial acetic acid
- (iii) 25 ml gum arabic solution (5%)
- (iv) 20 ml 0.275% chromeazurol S solution
- (v) 10 ml standard aluminium solution (111 $\mu\text{g Al/ml}$)

Slowly and carefully, with adequate stirring, add 1.8M ammonium hydroxide to bring the pH to 4.25 using a pH meter. Make up to 500 ml and filter through a No. 40 fluted filter paper. Add a few crystals of thymol to prevent mould growth.

D. *Calibration*

- (i) Into each of six stoppered measuring flasks (numbered 1-6) of 50 ml capacity pipette 2 ml of buffer solution (pH 4.25).
- (ii) Add standard fluoride solution to the flasks to give fluoride content as follows:

Flask No.	1	2	3	4	5	6
$\mu\text{g F}$	0	4	8	12	16	20
- (iii) Add to each 30 ml of water.
- (iv) Add 15 ml of aluminium-chromeazurol S stock solution to each flask, make up to the mark with water and mix well.
- (v) Heat on a water bath at 60° C for 15 minutes. Then cool to room temperature by placing in a bath of cold water.
- (vi) Measure the difference between the absorbancy of each fluoride containing solution and that containing none using a Hilger-Spekter absorptiometer with yellow green 605 filters and 2 cm cells, or a similar suitable instrument.
- (vii) Plot a calibration curve of the difference in absorbancy against fluoride concentration. Two typical calibrations are recorded in Table I.

INTERFERENCES

The system used in this method is basically the same as the aluminium-eriochrome-cyanin and aluminium-haematoxylin methods and it is therefore to be expected that the ions interfering with the present method would be the same, as was found with these methods.

RESULTS AND DISCUSSION

Two typical calibration curves for the method are shown in Table I, and Table II shows a series of recoveries under normal conditions of use. These figures give a good idea of the accuracy and reproducibility of the method. The overall standard deviation for the range 0-18 μg fluoride is 0.46 μg (this figure is taken from a forthcoming paper on a statistical comparison of fluoride methods). Thus 0.9 μg should just be detectable with certainty in 50 ml of final solution, and this amount of fluoride must be present in the amount of treated distillate taken for the determination. In the case of macrodistillation the volume of distillate after neutralization is of the order of 170 ml and about 30 ml of this can be used for fluoride determination. The sample must therefore contain a minimum of 5.4 μg of fluoride. In a macrodistillation there is no difficulty in handling 25 g of sample and this gives a limit of detection of fluoride of about 0.2 p.p.m.; the method is thus only about half as sensitive as the eriochrome-cyanin one. Using a microdistillation where the whole of the distillate can be used for the determination, and modifying the technique to keep dilution a minimum, the limit of detection can be lowered to 0.1 p.p.m. or less.

A similar method which uses the thorium chromeazurol complex has recently been published by REVINSON AND HARLEY⁴. The change in absorbancy obtained for 10 μg fluoride by these authors using the thorium salt appears to be only half that

TABLE I
TYPICAL CALIBRATIONS FOR THE ALUMINIUM CHROMEAZUROL METHOD

$\mu\text{g F}$	0	4	8	12	16	20
Absorbancy $\times 10^3$ a	0	124	227	327	437	540
b	0	125	234	328	444	538

TABLE II
TYPICAL RECOVERIES OF FLUORIDE (μg) BY THE ALUMINIUM CHROMEAZUROL METHOD

<i>F added</i>	<i>F recovered</i>	<i>F added</i>	<i>F recovered</i>
3.0	3.2	11.0	11.4
	3.2		10.9
	3.2		10.9
	3.0		10.9
	2.8		
	2.8	18.0	17.3
	3.0		17.6
	3.2		17.8
	2.9		18.1
	2.9		17.3
	2.3		18.0
11.0			18.1
	10.9		18.6
	11.4		17.5
	10.9		18.4
	11.3		18.0
	10.3		18.0
	10.4		17.2
	11.2		17.9
	11.9		17.8

obtained when the aluminium salt is used and the standard deviation of the former method seems to be somewhat larger than that using aluminium although no actual figure is quoted. The standing for two hours makes the thorium method considerably longer than the aluminium one but it is probable that the standing time of two hours quoted by REVINSON AND HARLEY could be considerably curtailed by employing a short period of heating as has been done by ourselves.

The mechanism of reactions involved in this method is expected to be similar to those put forward in our previous papers. A chelate compound is first formed between the dye ion and the aluminium which is subsequently destroyed by fluoride. Under the conditions of the method the aluminium and fluoride appear to be combined in the ratio 1:2 and the chelate compound appears to have the formula $\text{Al}(\text{dye})_2$.

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The Authors wish to thank Mr. A. S. NICHOLSON for his interest and encouragement.

SUMMARY

A spectrophotometric method for determining fluoride using the aluminium chromeazurol complex is described. Fluoride in solution free from interfering ions or obtained by distillation as hydrofluosilicic acid is determined by destruction of the complex, the amount destroyed being directly proportional to the fluoride present. The method will detect as little as $0.02 \mu\text{g/ml}$ of fluoride and with $0.20 \mu\text{g}$ in the final solution fluoride can be determined with an accuracy of $\pm 0.6 \mu\text{g}$.

References p. 456.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage de l'anion fluorhydrique au moyen du complexe aluminium-chromazurol-S. L'anion fluorhydrique, en l'absence d'ions gênants, ou séparé par distillation sous forme d'acide fluosilicique, est déterminé par décomposition du complexe, la quantité décomposée étant directement proportionnelle à la quantité de fluorure présent. Cette méthode permet de détecter jusqu'à $0.02 \mu\text{g/ml}$ de fluorure. Des quantités de F^- allant de 0 à $20 \mu\text{g}$ peuvent être dosées avec une précision de $\pm 0.6 \mu\text{g}$.

ZUSAMMENFASSUNG

Eine spektrophotometrische Methode für die Bestimmung des Fluorid-Anions mittels eines Aluminiumchromazurol-S Komplexes wird beschrieben. Das Fluorid-Anion wurde in Abwesenheit von störenden Ionen, oder abgetrennt mittels Destillation in Form von Fluorkieselsäure, durch Zersetzung des Komplexes bestimmt. Die Menge, welche zerstört wurde, war direkt proportional der Menge an Fluor. Diese Methode erlaubt Fluoridmengen bis zu $0.02 \mu\text{g/ml}$ nachzuweisen. Mengen von F^- zwischen 0-20 μg können mit einer Präzision von $\pm 0.6 \mu\text{g}$ bestimmt werden.

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INFLUENCE OF ORGANIC BASES ON THE PARTITION OF
INDICATOR ACIDS (AND VICE-VERSA) IN A WATER-CHLOROFORM
SYSTEM
ANALYTICAL APPLICATIONS

by

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In a series of previous papers¹ we discussed the ability of several indicator acids (A) to react with organic bases (B) yielding coloured compounds (BA) largely soluble in organic solvents, and we also explained how we can take advantage of the behaviour of those compounds in order to achieve the accurate titration of salts of organic bases in a water-chloroform system. The transformation interval of BA compounds (termed "amphindicators") *i.e.* the pH limits, between which a displacement of the colour occurs from one phase to the other, being connected to solubility problems², an attempt has been made to study quantitatively the influence of organic bases on the partition ratio of the indicator acids we are concerned with, in a water-chloroform system as a function of pH. Full advantage has been taken of the opportunities offered by these investigations, thanks to which it has been possible to further explore our subject by conversely studying the influence of indicator acids on the quantitative distribution of several organic bases between the above two solvents.

The first part of the present paper includes a brief description of the experimental path followed, the results obtained, and the general conclusions derived. The second part deals with a number of analytical applications based upon the above data.

From our previous qualitative investigations on the possible combinations of a dozen indicator acids with a dozen alkaloids it has been proved that generally speaking, all compounds of this type behave in an analogous fashion in the case we are dealing with. For this reason the following quantitative experiments were limited to only the compounds of bromothymol blue with the bases: procaine, strychnine, ephedrine, quinidine and atropine.

Influence of procaine base on the partition solubility of bromothymol blue (BTB) in a water-chloroform system

The partition of the dye between equal volumes of water and chloroform in various hydrogen-ion concentrations was determined first.

Reagents:

1. $5 \cdot 10^{-3}$ molar bromothymol blue stock solution

0.312 g of BTB (twice recrystallized from ethyl alcohol) is dissolved in a small mortar by adding 5 ml of 0.1N NaOH solution and further diluting with distilled water to 100 ml.

References p. 465.

2. Comparison standard scale

Prepared by diluting the above BTB stock-solution with 0.1N NaOH so as to obtain the following, decreasing by 10% dye concentrations:*

Test tube No. 1.	$2.50 \cdot 10^{-5}$ mol.	Test tube No. 9.	$1.08 \cdot 10^{-5}$ mol.
2.	$2.25 \cdot 10^{-5}$	10.	$0.97 \cdot 10^{-5}$
3.	$2.03 \cdot 10^{-5}$	11.	$0.87 \cdot 10^{-5}$
4.	$1.82 \cdot 10^{-5}$	12.	$0.78 \cdot 10^{-5}$
5.	$1.64 \cdot 10^{-5}$	13.	$0.71 \cdot 10^{-5}$
6.	$1.48 \cdot 10^{-5}$	14.	$0.64 \cdot 10^{-5}$
7.	$1.33 \cdot 10^{-5}$	15.	$0.57 \cdot 10^{-5}$
8.	$1.20 \cdot 10^{-5}$	16.	$0.51 \cdot 10^{-5}$

3. Full series of buffer mixtures differing by 0.2 pH units

The following solutions, the pH value of which were controlled potentiometrically, have been prepared:

From pH 1 to 3: pure hydrochloric acid solutions.

From pH 3 to 6: sodium citrate-HCl/NaOH solutions, according to SÖRENSEN.

From pH 6 to 8: KH_2PO_4 -NaOH solutions, according to CLARK AND LUBS.

From pH 8 to 9: boric acid-NaOH solutions.

From pH 9.2 to 11: soda-borax mixtures, according to KOLTHOFF.

From pH 11 to 12: Na_2HPO_4 -NaOH solutions, according to KOLTHOFF AND VLEESCHOUWER.

Experimental procedure

A mixture of 4.8 ml of the chosen buffer solution, 0.2 ml of the $5 \cdot 10^{-3}M$ BTB standard and 5 ml of chloroform was vigorously shaken in a small separator for one minute. The clear chloroform layer was transferred to a second separator and the dye retained by each solvent was determined as follows. The aqueous extract was diluted with 2N NaOH solution so that the colour of the liquid always fell between the limits of the standard scale, whereas the BTB dissolved in the chloroform was extracted by shaking with a suitable of 0.1N NaOH. By comparing the colour intensity of these two alkaline aqueous solutions with that of the standards, the BTB-molarity of each was found and the partition of the indicator between the two solvents at the chosen pH computed**. By this procedure $\pm 2\%$ accuracy was achieved, verified by checking the sum of the partial molarities found against the known total BTB-concentration of the system.

Curve J in Fig. 1 is a plot of the water solubility of BTB (expressed in percent) versus the corresponding hydrogen exponent.

We next investigated the influence of procaine base on the partition solubility of the indicator. This study was performed exactly as the preceding one, the only difference being that a suitable volume of $5 \cdot 10^{-3}M$ procaine hydrochloride solution was added to the system.

Curve A1/5 in the same graph shows the partition of BTB in the aqueous phase in the presence of a fifth of the equimolar procaine amount. Likewise, curves A1/4, A1/2, A3/4, A1, A2, A5, A10 and A50 correspond to a 0.25, 0.5, 0.75, 1, 2, 5, 10 and 50 base to acid ratio respectively.

* The above scale, if kept in a dark place in stoppered tubes, keeps its colour intensity for several weeks. Diffused sunlight, however, gradually destroys the dye, a discolouration being observable within a short while. Unalterable artificial comparison solutions can be obtained by dissolving 0.67 g of pure $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 50 ml of distilled water and diluting to a final volume of 100 ml with a 30% ammonia solution. The colour intensity of this standard corresponds to a $5 \cdot 10^{-5}M$ BTB solution (of pH 12), obeying Beer's law, within the limits of concentration we are interested in. By further diluting this stock solution with 10% ammonia, colour shades approaching those corresponding to the respective BTB molarities may be obtained.

** The colour of both layers depends on the pH of the aqueous phase. At pH's ranging over 3 the known BTB shades are observable in the H_2O -layer, varying from yellow to blue, whereas the pH must surpass the value 5.5 before any yellowish shade is perceivable in the chloroform, by which up to this pH the indicator acid is extracted in its undissociated lactonic form.

From these curves one sees that the procaine base substantially reduces the water-solubility of BTB, this effect being greater, the higher the base concentration with respect to that of indicator involved. This is in full agreement with our previous qualitative observations².

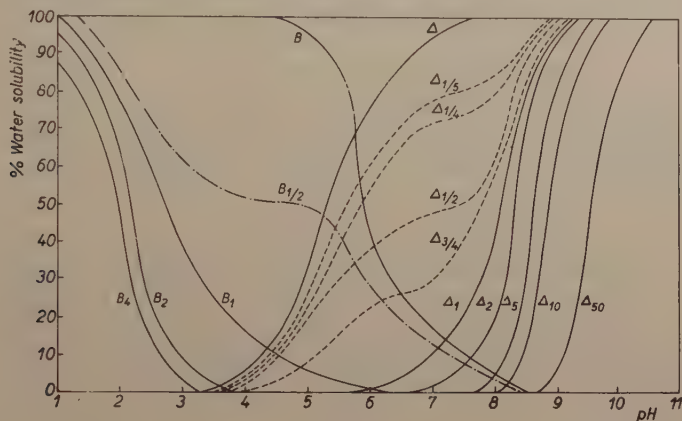


Fig. 1

What should receive the greatest emphasis when discussing this graph are the slopes characterizing the dotted curves, which correspond to the condition $[B]:[\Delta] < 1$. Indeed, the steepest points of these slopes coincide with the existing BTB excess in the aqueous phase. This leads us to the very important conclusion that under such concentration ratios, an amount of the available dye, *equimolar to the base added*, is extracted by the chloroform and, consequently, *that an indirect determination of the base could thus be possible by a colorimetric estimation of the dye dissolved in the organic phase*. By lessening the base to acid ratio, slopes become steeper, being slightly shifted towards the alkaline region, where the CHCl_3 -solubility of BTB, when no base is present, equals zero. Hence, $[B]:[\Delta] < 0.5$ should be the most favourable condition for an accurate determination of organic bases at pH 7.2. At higher pH ranges we noticed that a fraction of the BTB amount added, always equivalent to the theoretical values, could again be extracted by the organic solvent, but a larger concentration of indicator acid was required in this case.

Thus, we had at hand a simple method, which permitted us to further explore our subject matter by conversely studying the influence of bromothymol blue on the partition of several alkaloids between water and chloroform.

Influence of bromothymol blue on the partition of procaine base in a water-chloroform system

Using the above colorimetric method, experimental details of which are given on p. 462, we firstly plotted curve B (Fig. 1), illustrating the percentual partition of pure procaine between equal volumes of water and chloroform, as a pH function. The accuracy was easily checked by the sum of the two procaine concentrations found at different pH levels which approximated by $\pm 2\%$ the known base-molarity in the system.

Curves $B_{1/2}$, B_1 , B_2 and B_4 , in the same graph, plotted from the values obtained by adding to a constant amount of base 0.5, 1, 2 and 4 mol-equivalents of indicator acid, clearly reveal the influence of BTB on the partition solubility of procaine.

The slope of curve $B^{1/2}$ shows again that when A is less than B a quantity of base equimolar to the indicator acid added in the system is extracted by the chloroform as a BA compound at pH's at which, in the absence of BTB, the base is completely insoluble in this solvent. This behaviour, which is quite analogous to that observed in the opposite case could probably lead to further analytical applications.

Influence of bromothymol blue on the partition solubility of some other alkaloids and vice-versa

The partition of ephedrine, strychnine, atropine and quinidine, either alone, or in the presence of an equimolar amount of BTB, between equal volumes of water and chloroform, and finally the influence of the above bases on the solubility of the dye was investigated next, by applying the colorimetric procedure already outlined.

The results obtained are expressed graphically in Fig. 2, where curves ST^* , QD , AT , PR and EPH are a plot of the H_2O -solubility of strychnine, quinidine, atropine, procaine and ephedrine bases with change in pH. Curves ST_A , QD_A , AT_A , PR_A and EPH_A show the effect of one BTB moleq. on the partition of those alkaloids, and ΔPR , ΔEPH , ΔST , ΔAT , ΔQD , the influence of an equimolar amount of the respective alkaloids on the partition of the dye.

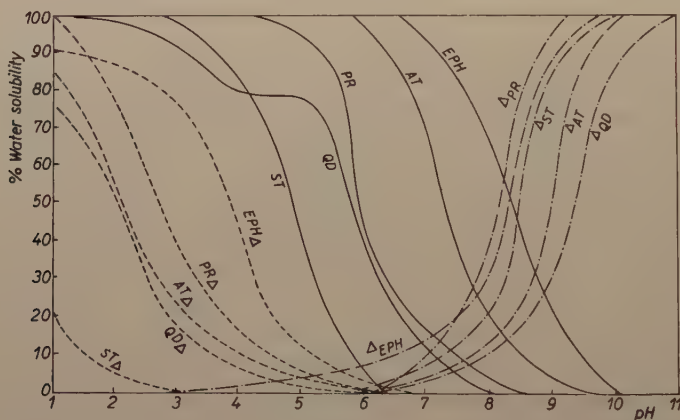


Fig. 2

This graph reveals that for every BA compound there exists a definite pH value only where the partition coefficients of both components are identical. Below and above this pH value each of them is partitioned according to its individual solubilities, the latter being greatly influenced by the presence of the second reactant. On the other hand, at pH areas neighbouring this value, where, as stated, $[B] = [A]$ in both phases, BA compounds are retained in a negligible proportion in the aqueous phase. This means that a direct titration of a given organic base is possible at said narrow pH intervals, if an aqueous A standard solution is used as the titrant, and reciprocally.

By increasing or decreasing of the H -ion concentration BA compounds undergo an "acidic" or "alkaline" decomposition. The latter particularly concerns their application in "amphimetry"^{1,2}.

* In carrying out our experiments with strychnine some anomalies have been encountered, due to the presence of hydrochloric acid in the buffer solution used. These anomalies, consisting of an abnormal decrease of the H_2O -solubility of strychnine were avoided by employing sulphuric instead of hydrochloric acid for buffer mixtures with pH values below 5.

APPLICATIONS

Direct titrimetric determination of alkaloids by means of indicator standard solutions

Many alkaloids and other organic bases can be directly titrated with an aqueous indicator acid standard solution. The titration must be performed in a water-chloroform system, the aqueous layer being so buffered as to restrict to a minimum the H_2O -solubility of the resulting *BA* compound. The appearance of a permanent colour in the aqueous phase indicates the end-point.

In some cases the titration may advantageously be carried out conversely, *i.e.* by pouring the solution under investigation into a measured volume of the indicator standard. In such cases, the end-point is noticed by a complete decolorization of the aqueous phase.

Obviously, the accuracy obtained by this method is higher, the less the water-solubility of the *BA* compound yielded.

Fig. 2 (p. 460) shows that the ephedrine, procaine, atropine, quinidine and strychnine tetrabromothymolphthaleinsulphonates exhibit a minimum water-solubility between pH 5.5 and 6.5. In fact, the above bases can be titrated with bromothymol blue in the presence of buffer mixtures with pH values lying within the above limits. The results are satisfactory; ephedrine shows a greater divergence from theory owing to its considerable water-solubility.

Procedure

0.2 ml of either an aqueous or chloroform solution of the base to be determined, are placed in a test-tube containing 2 ml of pH 5.5 buffer solution and 15 ml of chloroform. $1 \cdot 10^{-3}M$ bromothymol blue solution is run in with vigorous shaking of the mixture after each new addition of reagent. The *BA* compound, being thus extracted by the chloroform, imparts to the latter a bright yellow colour, whereas the water-phase, as far as the system contains an excess of organic base, remains colourless. The titration is interrupted as soon as a persistent yellowish shade is noticeable in the aqueous layer.

Besides bromothymol blue, we also employed several other indicators as titrants; *e.g.* quinine has been determined with bromophenol blue, strychnine with bromocresol green, *etc.*

This simple procedure is naturally of great interest especially for orientating purposes.

Indirect colorimetric method for the determination of alkaloids and other organic bases

As has been shown (p. 459), by adding an excess of an indicator acid to a suitably buffered solution containing an organic base, and by agitating the mixture with chloroform, the base is quantitatively extracted by the organic solvent as a coloured compound of the *BA*-type. Then, by separating the chloroform layer and decomposing the *BA*-compound by further shaking with a known volume of sodium hydroxide solution, we indirectly find out the required unknown base molarity by a colorimetric determination of the indicator, finally passing under its ionic form into the caustic solution*.

On applying this method the following points must be taken into consideration:
i. *Suitable indicator concentration:* For optical reasons the dye concentration of

* The dye extracted as *BA* by the chloroform could of course, be evaluated by comparing the colour intensity of the organic phase directly to a suitable standard scale. However, these solutions being generally of a yellow shade, are less appropriate for colorimetric work.

the final aqueous extract at the very moment of the colorimetric estimation should be between $1.0 \cdot 10^{-5}$ and $2.5 \cdot 10^{-5}$. More intensely coloured solutions can of course be diluted so as to fall within these favourable concentration limits.

In order to avoid excessive dilutions, which would multiply any error introduced in matching colour, it is advisable to accept as a suitable initial indicator concentration in the aqueous phase that of $4 \cdot 10^{-4}$, as offering logical experimental conditions.

2. *Rational buffering*: Obviously, the aqueous phase must be buffered so as to exclude any possibility of traces of the available indicator excess to be extracted by the chloroform. This condition is adequately met in the case of a $4 \cdot 10^{-4}M$ bromothymol blue solution by working at pH 7.6, whereas the "safe" pH values for $4 \cdot 10^{-4}M$ solutions of bromocresol green, bromophenol blue and thymol blue are 6.6, 5.6 and 5 respectively.

Thus, by adding to the solution containing the base to be determined 0.4 ml of $5 \cdot 10^{-3}M$ indicator standard, by buffering at the above pH values and finally by bringing the volume of both phases to 5 ml, one is sure that no trace of free indicator acid can be extracted by the organic solvent, especially since, owing to the presence of the base, the final dye concentration in the water layer is always less than $4 \cdot 10^{-4}$.

3. *Base concentration limits*. We know that at the said minimum allowable pH values the base can be quantitatively extracted by the chloroform only if $[B]:[A] < 0.5$. Hence the base concentration (H_2O -phase) must never exceed $4 \cdot 10^{-4}:2 = 2 \cdot 10^{-4}$. Of course, lower base concentrations are by no means detrimental. On the contrary they are desirable, especially in the case of relatively soluble organic bases.

We therefore must previously know the approximate base molarity of the sample in order to perform the determination under favourable concentration conditions. When nothing at all is known about $[B]$, the latter can easily be determined by the above titrimetric method.

Examples

Determination of procaine

As a first example of this application we give details of the technique we followed in studying the partition solubility of procaine (p. 459).

Procedure: 4.8 ml of the buffer chosen for each test were measured off in a small separator, 0.2 ml of $5 \cdot 10^{-3}M$ procaine hydrochloride solution plus 5 ml chloroform added and the mixture vigorously shaken for one minute.

Determination of the base dissolved in the chloroform layer

When both phases were limpid, the chloroform solution was quantitatively run off in a second separator, containing 0.4 ml of $5 \cdot 10^{-3}M$ bromothymol blue standard and 4.6 ml of pH 7.6 buffer solution. Then the mixture was vigorously agitated for one minute and the clear chloroform layer carefully transferred into a third separator. The aqueous solution of the second separator was washed out with 2-3 ml of pure chloroform and the washings, added to the main chloroform extract, further shaken with 10 ml of 0.1N NaOH solution. After discarding the colourless solvent, the blue aqueous solution was suitably diluted (depending on its colour intensity) and the procaine content evaluated by obtaining a colour match with one of the standards (p. 458).

Determination of the base dissolved in the water layer

The initial aqueous extract which was abandoned into the first separator was rendered strongly alkaline by adding 0.5-1 ml of 10% caustic soda, the organic base was twice extracted with 5 ml of pure chloroform and the total chloroform extract further treated as above.

The technique followed in studying the influence of BTB on the partition solubility of procaine was quite similar except that in this series of experiments both reactants were determined in each layer.

References p. 465.

Procedure: To 4.6 ml of the chosen buffer 0.2 ml of each $5 \cdot 10^{-3}M$ BTB and procaine hydrochloride solutions plus 5 ml of chloroform were added and the system thoroughly shaken for one minute. The chloroform layer was next treated in a second separator with the suitable volume of $1.0N$ NaOH solution. The dye fixed by the alkali was then directly estimated as usual, whereas the liberated procaine base was determined by further treating the chloroform layer with an excess of BTB at pH 7.6 as already described. On the other hand, the dye and base concentration of the initial aqueous layer were determined by adding a measured volume of NaOH solution, by extracting the procaine with chloroform, and continuing as previously.

Determination of procaine hydrochloride in an injectable solution of magnesium thio-sulphate

1. *Evaluation of the approximate molarity by a direct titration.* 0.1 ml of the sample was diluted with 2 ml of pH 5.4 buffer solution. By titrating in the presence of 10 ml chloroform, 1.75 ml of $1 \cdot 10^{-3}M$ BTB standard solution were consumed. Thus we found $1.75 \cdot 0.0002728 = 0.0004774$ g of procaine hydrochloride in 0.1 ml of liquid, a figure corresponding to the approximate molarity of $1.75 \cdot 10^{-2}$.

2. *Indirect accurate determination.* The liquid was diluted with an equal volume of distilled water. From this new solution, 0.1 ml was measured into a separator, 0.4 of $5 \cdot 10^{-3}M$ BTB standard (i.e. an excess of 114%), 4.5 ml of pH 7.6 buffer mixture and 5 ml of chloroform added, and the determination continued as already mentioned on p. 461. By diluting the final caustic extract to 40 ml and comparing the intensity of the colour to the standard scale, we found a BTB molarity of $2.25 \cdot 10^{-5}$. Hence the initial injectable solution contained:

$2.25 \times 40 \times 0.00002728 \times 2000 = 0.491$ of procaine hydrochloride per cent of liquid, i.e. 0.00982 g of this anaesthetic per 2 ml ampule (instead of the probable theoretical content of 0.01).

Determination of ephedrine in a potassium guaiacolsulphonate syrup

This dark-coloured preparation contained 6.5% of potassium guaiacolsulphonate, sugar, glycerine, etc., as well as 0.165% of ephedrine base as camphosulphonate.

1. *Direct orientating titration.* (1 ml of $1 \cdot 10^{-3}M$ BTB sol. = 0.00016523 g ephedrine alkaloid). 1.5 ml of $1 \cdot 10^{-3}M$ BTB standard were consumed by 2 ml of a solution, prepared by diluting 5.35 g of the syrup to 200 ml with distilled water. (Because of the yellow shade of the aqueous phase, due to the proper colour of the preparation, the titration was carried out at pH 7, in spite of the fact that at such a pH level lower results were to be expected. However, the end-point was easily perceivable by the appearance of a green colour in the aqueous layer.) Hence, the approximate molarity of our diluted solution was $0.25 \cdot 10^{-3}$, corresponding to a 0.1544% ephedrine content of the syrup.

2. *Indirect colorimetric determination.* 2 ml of the diluted liquid were brought into a small separator, 0.4 ml of $5 \cdot 10^{-3}M$ BTB solution (i.e. $[A]:[B] \cong 4$) and 2.6 ml of pH 7.6 buffer added and the mixture vigorously shaken for one minute with 5 ml of chloroform. The lower layer was quantitatively transferred into a second separator and the extracted ephedrine tetrabromothymolphthaleine-sulphonate decomposed by treating the chloroform solution with $0.1N$ NaOH. The total volume of the new aqueous layer brought finally to 40 ml had a colour concentration corresponding to a $1.33 \cdot 10^{-5}$ BTB-molarity. Consequently the syrup contained

$$\frac{0.0000165 \times 40 \times 1.33 \times 10000}{5.35} = 0.1655\% \text{ of ephedrine.}$$

Determination of strychnine in an injectable solution of strychnine sulphate, sodium glycerophosphate and sodium cacodylate

1. *Orientating titration* (1 ml $1 \cdot 10^{-3}M$ BTB = 0.0004285 g $(C_{21}H_{22}O_2N_2)_2H_2SO_4 \cdot 5H_2O$). 2 ml of the sample, buffered at pH 7 required 2.1 ml of our $1 \cdot 10^{-3}M$ BTB standard. Therefore, the requested base concentration was $1 \cdot 10^{-3} \times 1.05$, corresponding to an approximate strychnine sulphate content of 0.04499%.

2. *Indirect colorimetric determination.* To 0.5 ml of the sample, diluted with 4.1 ml of pH 7.6 buffer, 0.4 ml of $5 \cdot 10^{-3}M$ BTB standard solution was added (i.e. four times as much dye as theoretically required), plus 5 ml chloroform. After final dilution of the caustic H_2O extract to 40 ml, its blue colour intensity was found to be equivalent to a BTB molarity ranging $1.48 \cdot 10^{-5}$. Consequently, each ml of injectable solution contained 0.504 mg of strychnine sulphate (stated content: 0.5 mg).

Determination of amphetamine sulphate in a mixture of acetyl salicylic acid, caffeine and phenacetin

After weighing and powdering a number of tablets, mix an accurately weighed quantity of the homogeneous powder, equivalent to one tablet, with 10 ml distilled water, digest for 10 minutes with frequent stirring and filter or centrifuge. Transfer 1 ml of the clear liquid into a separator, containing 0.4 ml of $5 \cdot 10^{-3} M$ BTB standard solution, add some drops of 0.1N NaOH solution until the indicator turns a distinct green, make up the volume to 5 ml by adding 3.6 ml of pH 7.6 buffer solution and shake the mixture with 5 ml chloroform for one minute. Treat the $CHCl_3$ extract with 40 ml of 0.1N NaOH and compare the developed blue colour with the standard scale.

BTB molarity found $2 \cdot 10^{-5}$, corresponding to 0.003685 of amphetamine sulphate, *i.e.* $0.003685 \cdot 40 \cdot 10 : 1000 = 0.00147$ g of $(C_9H_{13}N)_2H_2SO_4$ in each tablet, instead of the stated amount of 0.0015.

By this method we successfully determined several other organic bases, using bromothymol blue as well as other indicator acids. Thus, quinine and strychnine have been accurately determined at pH 5.6 with bromophenol blue and at pH 3.2 with tropeolin OO, procaine, emetine, strychnine, quinine with thymol blue at pH 5, and so on.

The fact that we particularly occupied ourselves with bromothymol blue was not accidental. From another study dealing with the detection of alkaloids, (investigations in this connection are now in progress), we observed that generally speaking, this dyestuff yields BA compounds the water solubility of which is less than that of other indicator "BA"-salts. On the other hand the colour strength and the relative stability of the alkaline BTB solutions against light are additional advantages indicating the use of this dye. Other indicators, as for example bromophenol blue, alizarinesulphonic acid *etc.*, which undergo a photochemical decomposition in an interval of only a few hours, are unsuitable as standards for colorimetric purposes. Of course, either a natural or artificial standard is superfluous when a photometer or spectrophotometer is used to match colours. The fact, however, that by using trivial means, an experienced worker may obtain equal precision with the unaided eye, encouraged us to avoid the use of optical apparatus, especially since the simplicity of the method would then have been lost.

It is superfluous to point out the multiple advantage offered by this colorimetric method, the simplicity of which helped us to bring about the quantitative study of solubilities, as summarized in the first part of this paper. The above examples merely illustrate its application in pharmaceutical analysis. However, the proposed technique is widespread in its applicability and should offer invaluable services in toxicological investigations and generally in those cases where the isolation of minute quantities of an alkaloid is practically impossible to attain and/or its determination problematic by routine methods.

Reviewing the biochemical literature we recently found that other investigators had already determined several alkaloids using methods based on a similar principle. PRUDHOMME³ proposed the colorimetric determination of quinine in biological materials by treating the sample with eosin and by further extracting the coloured compound yielded with chloroform. BRODIE, UNDERFRIEND *et al.*⁴ used methyl orange for the estimation of cinchona alkaloids and other organic bases in plasma and urine, by measuring the colour intensity of the resulting dichlorethylene extract. MARSHALL AND ROGERS⁵ benefit by the property of bromothymol blue to yield with cinchona alkaloids colours extractable with benzene. SPINKS⁶ suggested the use of eosin and a mixture of chloroform-butanol as the extractant for the fluori-

metric evaluation of the drug "antricyde" in plasma. GETTLER AND SUNSHINE⁷, modifying BRODIE AND UNDERFRIEND's method, suggest the use of chloroform instead of dichloroethylene for the extraction of the coloured compound, *etc.*

It must be noted that all these methods are rather complicated and of a restricted applicability.

SUMMARY

The influence of organic bases on the partition of bromothymol blue between water of varying H-ion concentration and chloroform was studied quantitatively. A principle for the accurate determination of minute quantities of organic bases by a colorimetric procedure has been established by this research and by the method developed the reverse influence could further be investigated. A number of analytical applications follow.

RÉSUMÉ

L'influence des bases organiques sur la répartition du bleu de bromothymol entre l'eau à différents pH et le chloroforme a été étudiée quantitativement. Ces essais ont permis d'établir une méthode de dosage colorimétrique pour de faibles quantités de bases organiques et d'examiner l'influence de l'indicateur sur le comportement des bases. La description d'un certain nombre d'applications analytiques complète cet exposé.

ZUSAMMENFASSUNG

Der Einfluss von organischen Basen auf die Verteilung von Bromthymolblau zwischen Wasser von verschiedenen pH-Werten und Chloroform wurde quantitativ untersucht. Diese Versuche erlauben eine kolorimetrische Bestimmungsmethode für kleine Mengen von organischen Basen aufzustellen und den Einfluss des Indikators auf das Verhalten der Basen zu prüfen. Die Beschreibung einer Anzahl analytischer Anwendungen vervollständigt diese Arbeit.

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QUADRIVALENT URANIUM AS A REDUCING AGENT IN POTENTIOMETRIC TITRATIONS

I. ESTIMATION OF FERRIC AND CERIC SALTS

by

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Quadrivalent uranium was first suggested by VORTMANN AND BINDER¹ as a reducing agent in volumetric analysis. Recently BELCHER, GIBBONS AND WEST² applied uranous solutions for the direct potentiometric titration of some oxidizing agents. These authors considered that although the reagent can be used for the direct titration of ferric iron and other oxidants the reactions are sluggish at room temperature. They increased the rate of the reaction by titrating at 60° C. In view of this they concluded that the reagent possesses no advantage over other reductants and in most cases is less convenient. However, in view of the tendency of certain oxidants to degrade at high temperatures, the reactions can be carried out more advantageously in the cold, if the optimum conditions of acidity are chosen and if certain catalysts are present in the reaction medium.

In the following experiments we applied quadrivalent uranium for the direct potentiometric titration of several oxidants at room temperature either alone or in the presence of each other, taking into account the changes in the redox potential of the U^{+6}/U^{+4} system with acidity, a factor of major importance in these titrations.

EXPERIMENTAL

I. Preparation of solutions

Quadrivalent uranium was prepared by the reduction of uranyl sulphate solutions containing ~ 18 g UO_2SO_4 per litre and made 0.18N with respect to H_2SO_4 or 1N with respect to HCl, either electrolytically or in the Jones reductor using pure granulated zinc. For the electrolysis a cell was used similar to that previously described³. The electrolysis required a period of 2-4 h at a current density of 200-500 mA/cm². Under these conditions only U^{+4} was produced⁴. When zinc was used as the reductor care was taken to oxidize any U^{+3} formed, by bubbling air through the reduced solution for 5 minutes⁵.

II. Standardization of the uranous solutions

The reducing power of the solutions prepared in H_2SO_4 were checked by $KMnO_4$ following the procedure recommended by EWING AND ELDRIDGE⁶. In the presence of HCl, the solutions were standardized with $K_2Cr_2O_7$ prepared according to the recommendation of FURNESS⁷. In all cases the end-points were determined potentiometrically.

III. Stability of the uranous solutions

According to MCCOY AND BUNZEL⁸ the rate of oxidation of U^{+4} by atmospheric oxygen varies inversely with the square of the H^+ ion concentration in the solution. GUSTAVSON AND KNUDSON⁹

References p. 473.

inferred that in the presence of 30% H_2SO_4 the stability of U^{+4} was so great that it could be titrated in the presence of air. We extended these studies, taking into consideration the effect of other interfering factors. Samples of the solution in 0.1-18N H_2SO_4 were kept in loosely stoppered colourless or brown bottles or in the presence of metallic salts. The stability of the reagent was also studied, while bubbling air or oxygen at a rate of 200 bubbles per min through the solution. At suitable intervals samples were withdrawn by means of a pipette and titrated against standard KMnO_4 .

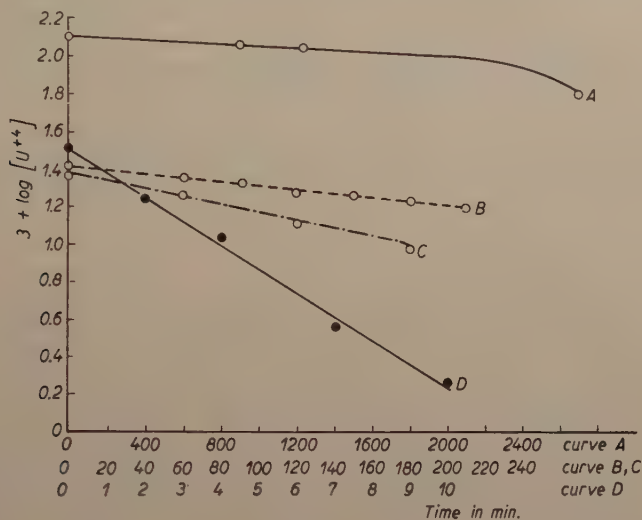


Fig. 1. (A) 0.125N U^{+4} in 5N H_2SO_4 , exposure to atmospheric oxygen;
(B) 0.02118N U^{+4} in 3N H_2SO_4 , bubbling air;
(C) 0.02250N U^{+4} in 5N H_2SO_4 , in the presence of KClO_4 ;
(D) 0.03328N U^{+4} in 3N H_2SO_4 , bubbling oxygen.

On plotting the logarithm of the U^{+4} concentration against time during exposure or while bubbling air or oxygen through, almost straight lines were obtained. By calculating the velocity constant of the reaction on the basis that it is one of first order, we obtained the k values recorded in Table I.

TABLE I

Normality of H_2SO_4	Condition of the reaction	Original concentration of U^{+4}	Velocity constant k
0.18	exposure to air in daylight	0.03375N	$1.67 \cdot 10^{-3}$
I	"	0.03313N	$1.2 \cdot 10^{-3}$
I	exposure to air (dark bottle)	0.03375N	$6.39 \cdot 10^{-4}$
5	exposure to air in daylight	0.1250N	$2.5 \cdot 10^{-4}$
5	exposure to air + Co^{+2}	0.04563N	$9 \cdot 10^{-4}$
5	" " " + Zn^{+2}	0.04063N	$1.39 \cdot 10^{-3}$
5	" " " + H_3PO_4	0.02938N	$3.8 \cdot 10^{-4}$
5	" " " + KCl	0.04188N	$6.1 \cdot 10^{-5}$
5	" " " + KClO_4	0.02250N	$4.0 \cdot 10^{-3}$
3	bubbling air	0.02118N	$1 \cdot 10^{-3}$
I	" "	0.02520N	$2.4 \cdot 10^{-3}$
3	" oxygen	0.03328N	$2.9 \cdot 10^{-1}$
I	" "	0.01875N	$3.5 \cdot 10^{-1}$

From these results the following conclusions could be drawn:

- (i) *Effect of acid concentration.* The stability of the solutions increased with the rise of acidity as revealed by the decrease in the k values. However, in the presence of $10N$ H_2SO_4 an exceptional decrease in concentration was observed after 5 days which could not be attributed to oxidation but to the separation of green crystals of uranous sulphate. The same phenomenon occurred with 15 and $18N$ H_2SO_4 when separation of the solid took place after a shorter period.
- (ii) *Effect of light.* In the absence of atmospheric oxygen light had no effect on the rate of oxidation, but in the presence of air the rate was greater in light than in the dark.
- (iii) *Effect of salts.* KCl and HCl increased the stability of the reagent. Zn^{+2} and Co^{+2} salts, enhanced its oxidation while phosphoric acid was of little effect. $KClO_4$ increased the tendency of the solution towards oxidation and the rate of oxidation was comparable with that found when air was passed into the solution at a rate of 200 bubbles per minute.

IV. *Solutions of the oxidants to be titrated, viz. ferricyanide, cupric copper, dichromate, permanganate, bromate, iodate and telluric acid* were made from the AnalaR or purified products by dissolving them in distilled water. Ferric and ceric solutions were prepared by dissolution in $0.1N$ HCl and $2N$ H_2SO_4 respectively. These solutions were standardized according to recommended procedures¹⁰.

V. The formal redox potential (E_f) of the U^{+6}/U^{+4} system

According to LUTHER AND MICHIE¹¹ the redox potential of the U^{+6}/U^{+4} system increases with rise of the H^+ ion concentration and with increasing ratio of (U^{+6}/U^{+4}) . MCCOY AND BUNZEL⁸ measured the E_f value in $0.125N$ H_2SO_4 as 0.615 V, whereas LUTHER AND MICHIE¹² gave 0.697 V. The E_o value as calculated from measurements in that acid amounts to 0.419 – 0.404 volt¹². Recently BELCHER, GIBBONS AND WEST² measured the redox potential at different pH values (HCl medium) and obtained values varying between 0.2 V at $pH = 1.5$ to ~ 0.500 V at $pH = -1$, which correspond to the acidity range $\sim 0.05N$ to $\sim 6N$ HCl . We extended our measurements to higher acidities both in the presence of HCl and H_2SO_4 . This was done by directly measuring the potentials set when a bright platinum electrode was placed in a solution containing equimolecular quantities of U^{+6} and U^{+4} in the presence of 0.1 to $10N$ HCl and 0.1 to $15N$ H_2SO_4 against the saturated calomel as a reference half-cell. As is apparent from the curves shown in Fig. 2 the redox potential amounts to 0.3 volt in the $0.1N$ acid. On increasing the acidity of 1 – $7N$

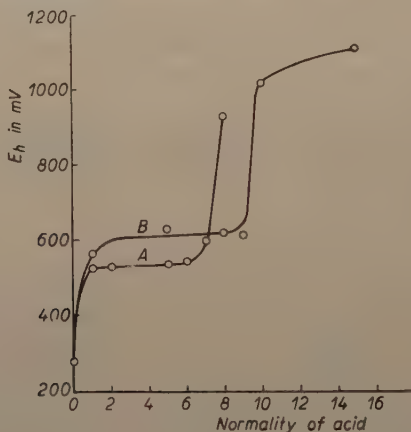


Fig. 2. (A) HCl ; (B) H_2SO_4 .

HCl , E_f rises to 0.53 V within which acidity range it remains practically constant but increases again to 0.9 volt in the presence of $9N$ HCl . In the presence of H_2SO_4 the potential of the U^{+6}/U^{+4} system increases from ~ 0.3 volt in $0.1N$ acid to 0.61 volt in 1 – $9N$ H_2SO_4 and increases thereafter to ~ 1 volt. Both curves are similar to that of BELCHER *et al.*² except above $7N$ HCl and $9N$ H_2SO_4 .

Estimation of ferric iron

BELCHER, GIBBONS AND WEST² found that titration of ferric iron with quadrivalent uranium is troublesome even at 60° and they preferred slow titration in the cold. However, as may be

seen from the results shown in Table II reduction of ferric chloride with U^{+4} yields good results in 0.1-7N HCl. The end-points are attained with inflections amounting to 55-27 mV per 0.1 ml of U^{+4} . The inflection decreases with rise of acidity such that with 9N HCl no apparent inflection was observed. Reduction also proceeds to completion in the presence of 0.36-2.7N H_2SO_4 . Ferric alum solutions could be titrated satisfactorily in the presence of 0.1N H_2SO_4 , 0.5-3.3N HCl and 2.7N HNO_3 .

TABLE II

Acidity	Max. inflection per 0.1 ml U^{+4} mV	Equilibrium time at end-point min	Theoretical end-point ml	Exptl. end-point ml	Error %
Titration of 5 ml 0.1408N $FeCl_3$ with 0.1389N U^{+4} solution					
Titration performed at 20° C					
0.1N HCl	43	5	5.07	5.09	+0.39
0.5N "	55	5	5.07	5.06	-0.19
3N "	47	8	5.07	5.08	+0.19
5N "	45	11	5.07	5.07	nil
7N "	27	14	5.07	5.06	-0.19
9N "	No characteristic inflection indicating end-point.				
Titration performed at 60° C					
5N HCl	27	1	5.07	5.05	-0.39
7N "	16	1	5.07	5.10	+0.59
Titration of 5.0 ml 0.1842N ferric ammonium sulphate with 0.1123N U^{+4} at 25° C					
1N H_2SO_4	77	1	8.20	8.16	-0.49
2N HCl	74	1	8.20	8.17	-0.37
2.7N HNO_3	72	5	8.20	8.15	-0.61

The reactions performed in the cold were found to take place rapidly at the beginning of the titration (needing ~ 1 min) but they take 5-8 min at the end-point, provided that the acidity does not exceed 3N. With 5 and 7N HCl the time increases to 11 and 14 min respectively at the end-point. At 60° C the reaction is rapid even at the higher acidities.

The nonreducibility of ferric iron in 9N HCl is readily interpretable on the basis that the formal potential of the Fe^{+3}/Fe^{+2} couple in 8N HCl as given by CARTER AND CLEWS¹³ (~ 0.79 V) is less than that of the U^{+6}/U^{+4} system (~ 0.9 volt) at the same acidity. At lower acidities the E_f values of the Fe^{+3}/Fe^{+2} system as computed from the titration curves amount to 0.675 V both in the presence of HCl and H_2SO_4 , which value is comparable to that of SMITH AND RICHTER¹⁴. The proximity of the E_f values of the U^{+6}/U^{+4} and the Fe^{+3}/Fe^{+2} systems, although permitting reduction of Fe^{+3} with U^{+4} does not permit the appearance of considerable jumps at the end-point unless the acid concentration in solution is kept at ~ 0.1 N. Representative titration curves are shown in Fig. 3.

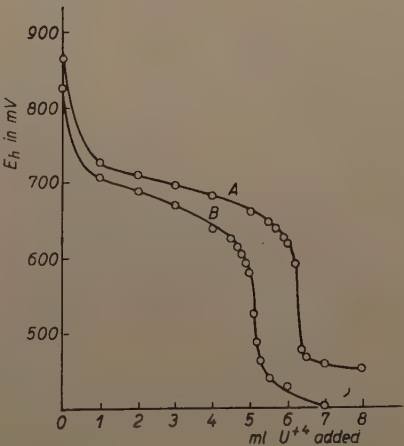


Fig. 3. (A) Titration of 10 ml 0.06446N Fe^{+3} in 0.1N H_2SO_4 with 0.102N U^{+4} (in 1N HCl); (B) Titration of 5 ml 0.1408N Fe^{+3} in 0.5N HCl with 0.1389N U^{+4} (in 0.18N H_2SO_4).

Estimation of ferricyanide

The E_0 value for the ferro-ferricyanide couple amounting to 0.36 volt¹⁵ does not permit the reduction of ferricyanide with U^{+4} . However, as may be visualized from the titration curves (Fig. 4), the formal potential amounts to 1 volt in 0.1N HCl and 1N H_2SO_4 . This together with E_f U^{+6}/U^{+4} in 1N H_2SO_4 and 0.1N HCl = 0.6 volt and 0.3 volt corresponds to a degree of completion = $2.96 \cdot 10^{-5}$ and $1.23 \cdot 10^{-8}$ in both acids. This denotes a greater tendency for the complex ferricyanide to be reduced than the ferric ions. However, in contrast to Fe^{+3} the time necessary for the attainment of equilibrium is larger as shown by BELCHER, GIBBONS AND WEST², varying from 10 min in 0.1N H_2SO_4 to 20 min in case of 0.1N HCl, to 60 min in 1N H_2SO_4 or 3N HCl.

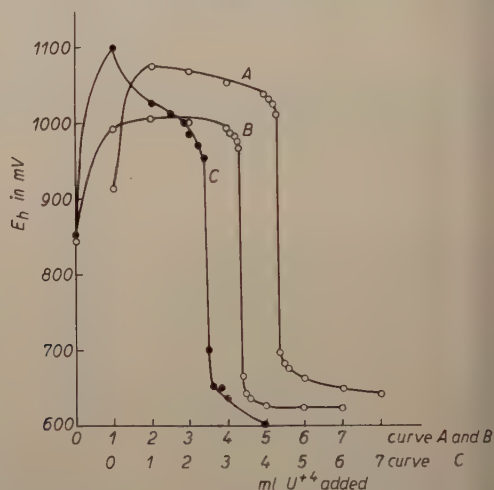


Fig. 4. Titration of 5 ml 0.1208N

$K_3[Fe(CN)_6]$ with U^{+4} :

- (A) in 0.1N HCl with 0.1389N U^{+4} at 25° C;
 (B) in 1N H_2SO_4 with 0.1389N U^{+4} at 25° C;
 (C) in 1.5N HCl with 0.1300N U^{+4} at 60° C.

The reaction is much accelerated on performing the titrations at 60° C when only 2-3 min are necessary, but then the errors are considerable. Even at that temperature, the time increases with rise of acidity to 7 and 12 min in 6N and 10N H_2SO_4 respectively. Good results are obtained when the titration is performed at room temperature. The reaction can be accelerated at the end-point by adding 2-3 drops of 0.1N ferric iron solution, in which case only one minute was found sufficient for equilibrium.

TABLE III

Acidity	Max. inflection per 0.1 ml U^{+4} mV	Equilibrium time at end-point min	Theoretical end-point ml	Exptl. end-point ml	Error %
Titration of 5.0 ml 0.1208N potassium ferricyanide with 0.1389N U^{+4} at 25° C					
0.1N H_2SO_4	130	10	4.35	4.37	+0.46
1N "	311	60	4.35	4.37	+0.46
0.1N HCl	322	20	4.35	4.34	-0.23
3N HCl	335	60	4.35	4.37	+0.46
6N HCl	160	60	5.95*	5.96	+0.17
Titration of 5.0 ml 0.1208N K-ferricyanide with 0.120N U^{+4} at 60° C					
0.1N H_2SO_4	229	3	5.03	2.86	-43.14
1N "	325	5	5.03	4.25	-15.51
4N "	280	2	5.03	4.32	-14.12
10N "	501	12	5.03	4.15	-17.49
16N "	No characteristic inflection indicating end-point				
0.5N HCl	254	3	5.03	3.48	-30.81
3N "	101	3	5.03	3.68	-26.84
7N "	134	5	5.03	4.32	-14.11

* $U^{+4} = 0.1015N$

References p. 473.

It should be noted that in the course of any titration, a yellowish precipitate is primarily formed which then passes through green to curdy white at the end-point. Such precipitations are possibly factors of major importance in causing the sluggishness of the reaction.

The titration curves in contrast to those of ferric iron are characterized by sharper inflections amounting to some hundreds of millivolts.

Estimation of ceric salts

The redox potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ system amounting to 1.61¹⁵ volts is sufficiently high to permit the reduction of ceric salts by quadrivalent uranium. The equilibrium constant and the degree of completion of these reactions as calculated from the formal redox potentials of the systems concerned (computed from Fig. 5), viz. $E_f \text{Ce}^{4+}/\text{Ce}^{3+} = 1.4$ volt and $E_f \text{U}^{6+}/\text{U}^{4+} = 0.6$

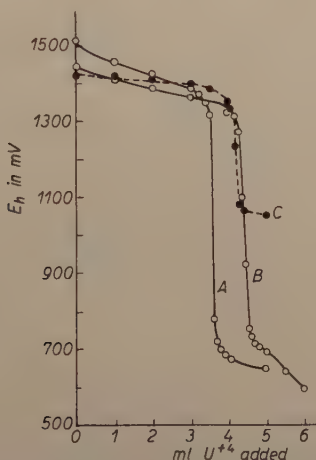


Fig. 5. Titration of 5 ml 0.0860N Ce^{4+} with U^{4+} :
(A) in 1N H_2SO_4 with 0.1183N U^{4+} at 60° C;
(B) in 1N H_2SO_4 with 0.0968N U^{4+} at 25° C;
(C) in 7N H_2SO_4 with 0.1012N U^{4+} at 60° C.

volt in 1N H_2SO_4 , amount to $7.2 \cdot 10^{-27}$ and $9 \cdot 10^{-10}$ respectively. Reactions performed in presence of HCl are susceptible to considerable errors owing to the liberation of chlorine, but provided that the reactions are performed in the cold and the acid concentration does not exceed 6N HCl, good results could be obtained. Although the reaction is rapid at the beginning of the titration yet it needs ~ 10 minutes at the end-point. It could be accelerated by the addition of ferric iron such that it takes only 3 minutes for the attainment of equilibrium. The time of reaction is also reduced by performing the titration at 60° C, when good results are obtained in solution containing up to 7N H_2SO_4 . At this temperature in the presence of HCl (1N or above) and H_2SO_4 concentration greater than 7N the errors become considerable. The cold titration in the presence of the ferric iron catalyst is more advantageous.

As is apparent from Fig. 5, the titration curves are smooth with sharp inflections at the end-points.

Reduction of cupric copper

The redox potential of the $\text{Cu}^{2+}/\text{Cu}^+$ couple amounts to 0.16 volt as compared with 0.46¹⁵ volt for the system $\text{Cu}^{2+}/\text{CuCl}_2^-$. Both values are less positive to the formal potential of the $\text{U}^{6+}/\text{U}^{4+}$ system in 1N acid and hence reduction of Cu^{2+} is not possible even when cuprous copper is complexed as CuCl_2^- . In conformity with this the titration curves are gradual without the appearance of an inflection characterizing the end-point.

Titration of ceric and ferric ions in a mixture of both

The redox potentials of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ systems amounting to 1.61 and 0.771¹⁵ are sufficiently widely separated from each other, thus permitting the reduction of both in two sharply-defined steps. The reaction occurs so rapidly in the presence of 0.36N H_2SO_4

that it needs only 2 min at both end-points for the attainment of equilibrium. The inflections at the end-points amount to 4.28 and 60 mV at the ceric and ferric stages respectively (*cf.* Fig. 6, curve A). The experimental end-points coincide fairly well with the theoretically calculated values.

TABLE IV

Acidity	Max. inflection per 0.1 ml U^{+4} mV	Equilibrium time at end-point min	Theoretical end-point ml	Exptl. end-point ml	Error %
Titration of 5.0 ml 0.086N ceric sulphate with 0.0968N quadrivalent uranium at 25° C					
1N H_2SO_4	349	10	4.44	4.43	-0.23
7N "	251	9	4.44	4.43	-0.23
11N "	181	9	4.44	4.43	-0.23
14.5N "	77	10	4.44	4.42	-0.45
1N HCl	271	10	4.44	4.43	-0.22
3N "	261	10	4.44	4.44	nil
8N "	No characteristic inflection indicating end-points.				
Titration of 5.0 ml 0.086N ceric sulphate with 0.1204N U^{+4} at 60° C					
1N H_2SO_4	533	3	4.20	4.17	-0.71
14.5N "	86	3	4.20	3.70	-11.91
3N HCl	333	3	4.20	3.49	-16.90
1N "	462	3	4.20	4.1	-2.38

Titration of vanadate and ferric iron

Similar to the ceric-ferric mixture the vanadate-ferric mixture could be reduced by U^{+4} in two well-defined steps (Fig. 6, curve B). The redox potential of the V^{+5}/V^{+4} system is higher than the Fe^{+3}/Fe^{+2} system by 0.23 V, a difference which is sufficient for a successful titration. The experimental end-points coincide with the theoretical values. Although the inflection at the ferric stage did not differ from that of ferric in the ceric-ferric mixture or in pure ferric solution, the inflection at the vanadate is smaller than that of vanadate alone¹⁸.

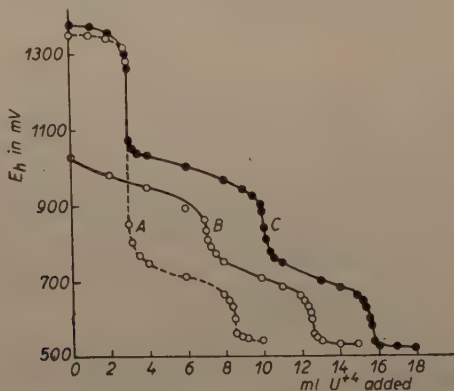


Fig. 6. (A) Titration of 5 ml 0.0481N Ce^{+4} + 5 ml 0.0859N Fe^{+3} with 0.0788N U^{+4} ;
(B) Titration of 5 ml 0.1083N V^{+5} + 5 ml 0.0874N Fe^{+3} with 0.0788N U^{+4} ;
(C) Titration of 5 ml 0.0481N Ce^{+4} + 5 ml 0.1083N V^{+5} + 5 ml 0.0874N Fe^{+3} with 0.0788N U^{+4} .

Titration of vanadate, ceric and ferric mixture

As may be seen from Fig. 6, curve C, the titration of this mixture with U^{+4} proceeds in 3 steps each characterized by a distinct inflection. At the ceric stage the inflection is sharper than the

other two, amounting to 189 mV as compared with 35 and 49 mV at the vanadate and ferric stages.

The experimental results do not deviate considerably from the theoretical end-points, and the reaction proceeds rapidly.

The rapidity of the reactions in the above mixtures is due in part to the low acidities in which the titrations were performed (0.36N H_2SO_4) and in part to the catalytic action of ferric iron.

ACKNOWLEDGEMENT

The authors wish to express their thanks to Prof. Dr. A. RIAD TOURKY for his interest in this work.

SUMMARY

Quadrivalent uranium is found to be a suitable reducing agent in potentiometric titrations, for the estimation of ferric and ceric salts. The stability of the reagent increases by raising the acidity and becomes considerable in the presence of HCl. The stability is not seriously affected by H_3PO_4 although Zn^{+2} and Co^{+2} ions enhance its oxidation. Light affects the stability of the reagent only in the presence of air.

The redox potential varies with acidity, being 0.3 volt at 0.1N HCl or H_2SO_4 rising to 0.53 or 0.61 in 1.7N HCl or 1.9N H_2SO_4 and increasing thereafter to ~ 1 volt.

RÉSUMÉ

L'uranium(IV) peut être utilisé comme réducteur, pour le dosage potentiométrique des sels de fer(III) et de cérium(IV). La stabilité du réactif augmente avec l'acidité; elle est très grande en présence de HCl; elle n'est pas très influencée par H_3PO_4 ; par contre Zn^{+2} et Co^{+2} favorisent l'oxydation. Quant à l'influence de la lumière, elle ne se manifeste qu'en présence d'air. Le potentiel rédox varie avec l'acidité: 0.3 V pour HCl ou H_2SO_4 0.1N, 0.53 ou 0.61 V pour HCl 1 à 7N ou H_2SO_4 1 à 9N et environ 1 V pour des acidités supérieures.

ZUSAMMENFASSUNG

Uran(IV) kann für die potentiometrische Bestimmung von Eisen(III) und Cer(IV)-Salzen als Reduktionsmittel gebraucht werden. Die Haltbarkeit des Reagenzes verbessert sich mit ansteigender Säurekonzentration; sie ist sehr gross bei Anwesenheit von HCl, wird aber durch H_3PO_4 nur wenig beeinflusst. Dagegen begünstigen Zn^{+2} - und Co^{+2} -Ionen die Oxydation. Was den Einfluss des Lichtes betrifft, so ist dieser nur bei Gegenwart von Luft festzustellen. Das Redoxpotential verändert sich je nach der Säurekonzentration: 0.3 V für 0.1N HCl oder H_2SO_4 , 0.53 V oder 0.61 V für 1 bis 7N HCl oder 1.9N H_2SO_4 und ungefähr 1 V für höhere Säurekonzentrationen.

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QUADRIVALENT URANIUM AS A REDUCING AGENT IN POTENTIOMETRIC TITRATIONS

II. ESTIMATION OF DICHROMATE, PERMANGANATE, BROMATE AND TELLURATE

by

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In the previous paper we studied the reduction of ferric iron, ferricyanide and ceric salts with quadrivalent uranium either alone or in the presence of each other. In this paper we applied the reagent for the estimation of dichromate, permanganate, tellurate, and bromate ions separately or in a mixture containing them together with ferric and ceric salts.

EXPERIMENTAL

I. Estimation of dichromate

BELCHER, GIBBONS AND WEST¹ studied the reduction of dichromate with U^{+4} and found that the reaction was sluggish at room temperature making the end-point rather indistinct, but when the titration was carried out at 60° C satisfactory and consistent results were obtained. We performed the titrations in the cold both in the presence of HCl and H_2SO_4 of various concentrations and in the presence of ferric iron as a catalyst. The reaction in the presence of 0.7N H_2SO_4 alone was rapid, needing only ~ 2 minutes for the attainment of equilibrium at the end-point. However, the time increased with rise of acidity (see Table I) so that it takes at the end-point 5 min and 40 min in presence of 3.6N and 14N H_2SO_4 respectively. In the presence of HCl the reaction is

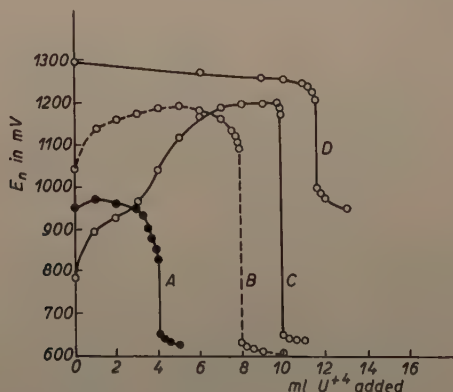


Fig. 1. Titration of 0.100N $K_2Cr_2O_7$ with U^{+4}

- (A) 5 ml $K_2Cr_2O_7$ in 3.6N $H_2SO_4 \times 0.125N U^{+4}$ (in 0.36N H_2SO_4)
- (B) 10 ml $K_2Cr_2O_7$ in 3.3N HCl $\times 0.125N U^{+4}$ (in 1N HCl)
- (C) 10 ml $K_2Cr_2O_7$ (aqueous) $\times 0.100N U^{+4}$ (in 1N HCl)
- (D) 4 ml $K_2Cr_2O_7$ in 20N $H_2SO_4 \times 0.03451N U^{+4}$ (in 0.36N H_2SO_4)

rapid only if the acidity is less than 2*N* when it takes ~ 2 min at the end-point. The time increases to 5 and 10 min when the acid concentration is raised to 4 and 10*N* HCl respectively. However, in presence of few drops of ferric chloride the reaction velocity is increased at the higher acidities. The decrease in the reaction rate at higher acidities is apparently due to the rise in the E_f of the U^{+6}/U^{+4} system, which in 14*N* H_2SO_4 approaches the formal redox potential of the Cr^{+6}/Cr^{+3} couple (~ 1.1 volt).

Oxidation of U^{+4} with $Cr_2O_7^{2-}$ occurs rapidly in presence of 2.5-5*N* HCl and 3.6*N* H_2SO_4 ; the results are quite satisfactory. The degrees of completion of the reactions as calculated using the E_f value of the Cr^{+6}/Cr^{+3} system in 1-7*N* HCl or 2*N* H_2SO_4 as ~ 1.11 volt and that of the U^{+6}/U^{+4} system as 0.53 and 0.6 volt in both acids, amount to $5 \cdot 10^{-14}$ and $4.3 \cdot 10^{-11}$ respectively.

Representative titration curves are shown in Fig. 1. Curve C represents the titration of neutral dichromate solution with U^{+4} (in 1*N* HCl). The curve exhibits an initial rise in potential due apparently to increase in the E_f value of the Cr^{+6}/Cr^{+3} system with rise of acidity. When the end-point is reached a sudden drop in potential occurs amounting to 400-500 mV. However, in the presence of an initial concentration of H_2SO_4 or HCl (curves A, B and D, Fig. 1) the rise in potential observed in the absence of acid decreased or disappeared completely.

TABLE I

Acidity	Normality of U^{+4}	Max. inflection per 0.1 ml U^{+4} mV	Theoretical end-point ml	Exptl. end-point ml	Error %
Titration of 0.1 <i>N</i> $K_2Cr_2O_7$ with U^{+4}					
0.1 <i>N</i> HCl	0.100 <i>N</i>	532	10.0	9.95	-0.5
0.5 <i>N</i> "	0.06667 <i>N</i>	147	7.5	7.45	-0.66
1.4 <i>N</i> "	0.1087 <i>N</i>	106	4.6	4.63	+0.65
2.0 <i>N</i> "	0.03379 <i>N</i>	348	11.83	11.77	-0.52
4.0 <i>N</i> "	0.03379 <i>N</i>	928	11.83	11.92	+0.75
6.0 <i>N</i> "	0.03379 <i>N</i>	823	11.83	11.83	nil
0.7 <i>N</i> H_2SO_4	0.03605 <i>N</i>	462	13.87	13.83	-0.29
3.6 <i>N</i> "	0.1670 <i>N</i>	158	3.00	3.02	+0.67
7.2 <i>N</i> "	0.03451 <i>N</i>	464	11.59	11.57	-0.17
14.4 <i>N</i> "	0.03451 <i>N</i>	464	11.59	11.57	-0.17
21.9 <i>N</i> "	0.03451 <i>N</i>	447	11.59	11.53	-0.51

II. Titration of ceric, dichromate, vanadate and ferric solutions in presence of each other

(A) The redox potentials of the Ce^{+4}/Ce^{+3} and the Cr^{+6}/Cr^{+3} systems are not sufficiently removed from each other to permit the titration of the ceric and dichromate ions in two sharply separable steps. The formal redox potential of the Ce^{+4}/Ce^{+3} system in 1*N* HCl amounts to 1.34 volt as compared with 1.1 for the Cr^{+6}/Cr^{+3} at the same acidity.

Fig. 2, curve A, represents the titration of a solution having 0.0574 *N* Ce^{+4} and 0.100*N* Cr^{+6} content, titrated with 0.09259*N* U^{+4} , the reaction medium being approximately 1.5*N* HCl. The titration curve is characterized by a single steep inflection amounting to 460 millivolts per 0.1 ml reagent which corresponds to a total experimental end-point at 8.47 ml of U^{+4} , thus agreeing fairly well with the required value for the titration of both solutions ($3.10 + 5.40 = 8.50$ ml of reagent).

(B) Titration of dichromate and ferric solutions in the presence of each other, appears feasible as already reported by BELCHER, GIBBONS AND WEST¹; because there is a sufficiently wide difference between their redox potentials at varying acidities amounting to 0.43 volt. Fig. 2, curve B shows a representative titration curve of a mixture containing 0.100*N* $K_2Cr_2O_7$ and 0.09971*N* $FeCl_3$ titrated with 0.1020*N* U^{+4} in the presence of 1*N* HCl. The curve is characterized by two inflections; the first amounting to 0.4 volt occurs 0.36% later than the end-point of the dichromate and the second amounting only to 52 mV occurs 0.2% later than the end-point of the ferric chloride. The same accuracy is encountered when the concentration one of the constituents is twice that of the other.

(C) Titration of dichromate and vanadate with 0.079 U^{+4} also gave rise to a curve with one single inflection corresponding to the reduction of both constituents, owing to the proximity of their redox potentials. The end-point differs only by 0.14% from the sum of the volume of U^{+4} equivalent to the constituents of the mixture.

(D) In the titration of dichromate, vanadate and ferric mixture only Fe^{+3} could be titrated in a separate step. The two others are reduced simultaneously as in the mixture of dichromate and vanadate. The titration curve of the mixture is characterized by two inflections, the first corresponding to dichromate and vanadate and the other to the ferric solution. Both inflections coincide fairly well with the theoretical end-points.

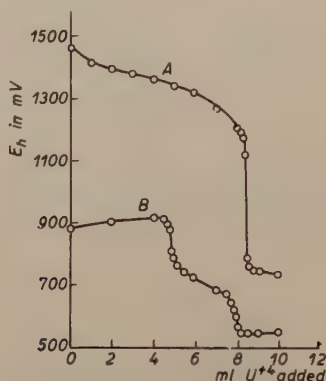


Fig. 2. (A) 5 ml 0.100N $\text{K}_2\text{Cr}_2\text{O}_7$ + 5 ml 0.0574N Ce^{+4} \times 0.09259N U^{+4}
(B) 5 ml 0.06446N Fe^{+3} + 5 ml 0.100N $\text{K}_2\text{Cr}_2\text{O}_7$ \times 0.1020N U^{+4}

III. Reduction of permanganate

(A) In acid medium

According to EWING AND ELDRIDGE², the oxidation of U^{+4} is best performed in 2N H_2SO_4 . We obtained good results also in the presence of 0.1-0.3N H_2SO_4 (see Table II). The titration curves are characterized by sharp inflections amounting to 300-400 mV and the end-points obtained potentiometrically do not deviate under these conditions from the visual ones.

TABLE II
TITRATION OF U^{+4} WITH KMnO_4

Acidity	Max. inflection per 0.1 ml KMnO_4 mV	Normality of U^{+4}	Normality of KMnO_4	Theoretical end-point	Exptl. end-point	Error %
0.1N H_2SO_4	415	0.1123	0.1422	7.9	7.88	-0.25
0.32N "	282	0.008886	0.01097	4.07	4.05	-0.5

Reduction of KMnO_4 was performed by BELCHER, GIBBONS AND WEST¹ at 60° C. They avoided low results due to the presence of HCl by adding Zimmermann-Reinhardt solution. In this investigation we carried out the titrations in presence of H_2SO_4 in the cold. Reduction of aqueous KMnO_4 with U^{+4} (in 0.18N H_2SO_4) leads first to the separation of MnO_2 ; this then redissolves and undergoes further reduction to Mn^{+2} . The end-points are attained somewhat early due to incomplete reduction of the deposited MnO_2 . Under these conditions the titration curve (Fig. 3) is characterized by two inflections, one (a) corresponding to the reduction of KMnO_4 to MnO_2 and the other (b) to the reduction of MnO_2 to Mn^{+2} . Curve B (Fig. 3) shows the course of the reaction, when at point b the solution is made 0.2N with respect to H_2SO_4 .

Better results could be obtained in presence of an initial acidity of 0.1-0.56N H_2SO_4 , provided that U^{+4} is not too dilute. In 0.7-2N H_2SO_4 the separation of MnO_2 is inhibited and the end-points coincide with the calculated values. At higher acidities than 3N H_2SO_4 the end-points are attained earlier than the theoretical values, and the errors increase with rise of acidity, owing apparently to loss of oxygen on decomposition. At such acidities the colour of KMnO_4 disappears before the potentiometric end-point is attained. The reaction velocity was found to vary appreciably

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with acidity. Thus, while it proceeds rapidly in 0.72*N* H₂SO₄, it takes 7-10 min in 1.4*N* H₂SO₄ and 20-30 min in 3.6*N* H₂SO₄ at the end-point. Although this time could be decreased to only 5 minutes by adding Ni(NO₃)₂ in the presence of 1.4*N* acid, the catalyst had but little effect at the higher acidities. However, ferric iron was found to enhance the reaction considerably at all acidities.

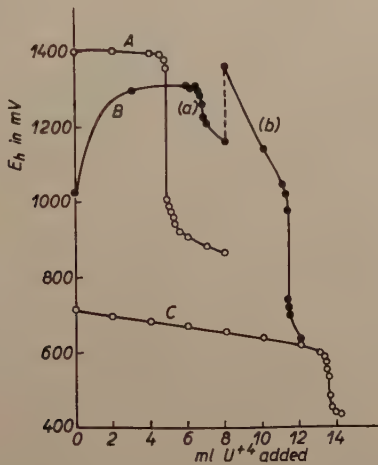


Fig. 3. (A) Titration of 5 ml 0.01097*N* KMnO₄ in 1.4*N* H₂SO₄ × 0.01133*N* U⁺⁴
(B) Titration of 10 ml 0.1422*N* KMnO₄ × 0.1251*N* U⁺⁴
(C) Titration of 25 ml 0.103*N* KMnO₄ in 2.5*N* NaOH × 0.1144*N* U⁺⁴ (in 0.2*N* H₂SO₄,

From the theoretical point of view, reduction of KMnO₄ with U⁺⁴ in acid medium is quantitative. The equilibrium constant and the degree of completion of the reaction as calculated using *E*_f(U⁺⁶/U⁺⁴) values as shown in Fig. 1 (Part I) and the *E*_f MnO₄⁻/Mn⁺² values as computed from the titration curves, viz.

normality of H ₂ SO ₄	0.1	0.5	1	4	8	12	<i>N</i>
<i>E</i> _f	1.35	1.40	1.42	1.42	1.42	1.45	volt
amount to 2.5·10 ⁻¹⁸⁶ and 4.3·10 ⁻²⁰ respectively at 1 <i>N</i> H ₂ SO ₄ .							

TABLE III

Acidity	Normality of U ⁺⁴	Volume and normality of KMnO ₄	Max. inflection per 0.1 ml U ⁺⁴ mV	Theoretical end-point ml	Exptl. end-point ml	Error %
0.1 <i>N</i> H ₂ SO ₄	0.1251	10 ml 0.1422	268	11.37	11.33	-0.34
0.72 "	0.0076	1 " 0.1009	261	13.33	13.33	nil
0.72 "	0.01133	5 " 0.01077	391	4.24	4.23	-0.21
1.44 "	0.00597	1 " 0.1009	277	16.90	16.93	+0.18
1.44 "	0.0156	2 " 0.1009	370	12.95	12.91	0.31
2.88 "	0.01589	5 " 0.01097	378	5.18	5.16	0.34
3.5 "	0.1237	5 " 0.1422	639	5.75	5.58	-2.96
7.2 "	0.02935	2 " 0.1009	638	7.4	6.3	-14.86
aqueous	0.1815	5 " 0.098	514	2.73	2.67	-2.2

(B) In alkaline medium

Reduction of KMnO₄ in alkaline medium yields MnO₄⁻² which becomes further reduced to MnO₂. The reaction could be checked at the MnO₄⁻² stage if the reducing power of the titrant is not very strong and if sufficient Ba⁺² ions are present to precipitate BaMnO₄. This was not the case with U⁺⁴, possibly owing to the strong reducing power of the reagent in the alkaline

medium as suggested by BELCHER, GIBBONS AND WEST¹, the reaction always passing partially to MnO_2 as is apparent from the late end-points. Accordingly, the titration of KMnO_4 with U^{+4} was made in 1.5-3*N* NaOH in absence of Ba^{+2} ions, using uranous solutions containing little acid ($\sim 0.1N$) and kept in a Zintl storage apparatus under CO_2 . Reduction of MnO_4^- passed under these conditions completely to MnO_2 , without the appearance of an inflection at the MnO_4^{+2} stage (curve C, Fig. 3).

The end-points are attended with reasonable inflections amounting to 50 mV and deviate but slightly from the calculated values. At alkalinities higher than 3*N*, although a small inflection appears at the manganate state, yet reduction always gives rise to the MnO_2 from the early stages. Under these latter conditions the end-points are attained earlier than the theoretical owing apparently to the autodecomposition of KMnO_4 . Since no values are known for the $E_f \text{U}^{+6}/\text{U}^{+4}$ couple in alkaline medium we calculated from free energy data³, the value -0.16 volt for $E_{\text{O}_3(\text{OH})}$ of the UO_3/UO_2 couple. This, together with $+0.588$ volt for the $\text{MnO}_4/\text{MnO}_2$ system, yield for K and a the values $5.2 \cdot 10^{-78}$ and $3.5 \cdot 10^{-16}$ which indicate a quantitative reaction between KMnO_4 and U^{+4} in alkaline medium (see Table IV)

TABLE IV

Alkalinity	Max. inflection per 0.1 ml U^{+4} mV	Theoretical end-point ml	Exptl. end-point ml	Error %
Titration of 10 ml 0.1422 <i>N</i> KMnO_4 with 0.1055 <i>N</i> U^{+4}				
1.5 <i>N</i> NaOH	47	8.09	8.07	-0.24
2 <i>N</i> "	47	8.09	8.08	-0.12
3 <i>N</i> "	125	8.09	8.07	-0.24
Titration of 0.103 <i>N</i> KMnO_4 with 0.1144 <i>N</i> U^{+4}				
2.5 <i>N</i> NaOH	51	13.5	13.55	+0.37

IV. Titration of permanganate in admixture with ferric, dichromate, vanadate and ceric ions

(A) The titration of KMnO_4 and Fe^{+3} was performed in the presence of 0.3*N* H_2SO_4 in order to avoid the action of HCl on permanganate. Owing to the great difference in the potential of the two systems, the mixture gives on titration two distinct separable inflections which occur in the region of the theoretical end-points (see Fig. 4, curve A). The equilibria were attained rapidly at the first inflection but needed 2-5 minutes for the attainment of equilibrium at the second end-point.

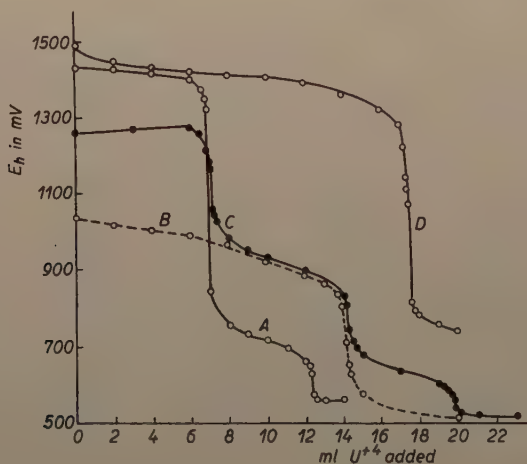


Fig. 4. (A) 5 ml 0.111*N* KMnO_4 + 5 ml 0.0843*N* Fe^{+3} \times 0.0788*N* U^{+4}
 (B) 5 ml 0.100*N* $\text{K}_2\text{Cr}_2\text{O}_7$ + 5 ml 0.1073*N* V^{+5} \times 0.073*N* U^{+4}
 (C) 5 ml 0.111*N* KMnO_4 + 5 ml 0.1083*N* V^{+5} + 5 ml 0.0874*N* Fe^{+3} \times 0.07737*N* U^{+4}
 (D) 5 ml 0.1066*N* KMnO_4 + 5 ml 0.1*N* $\text{K}_2\text{Cr}_2\text{O}_7$ + 5 ml 0.0481*N* Ce^{+4} \times 0.073*N* U^{+4}

(B) Curve B Fig. 4 represents the titration of a mixture containing dichromate and vanadate with U^{+4} . Owing to the proximity of the formal redox potentials of the Cr^{+6}/Cr^{+3} system (~ 1.11 V) and the V^{+5}/V^{+4} (~ 1 V)⁴, reduction of both constituents takes place at one step corresponding to the sum of the separate end-points.

(C) The mixture composed of $KMnO_4$, V^{+5} and Fe^{+3} gives rise to a titration curve characterized by 3 inflections (curve C, Fig. 4), the first amounting to 112 mV corresponds to the reduction of $KMnO_4$ and occurs 0.14% early, the second amounting to 59 mV corresponds to the reduction of V^{+5} and occurs 0.29% early, the third inflection amounting again to 18 mV is that of the Fe^{+3} and occurs 0.35% late. The end-points do not deviate appreciably from the theoretical end-points.

(D) The redox potentials of the MnO_4^-/Mn^{+2} and the Ce^{+4}/Ce^{+3} amounting to 1.52 and 1.61 volts are so close that titration of each constituent alone is not possible. The titration curve possesses only a single inflection amounting to 500 mV per 0.1 ml of U^{+4} . The experimental end-point coincides fairly well with the sum of the theoretical values. The ceric-permanganate-dichromate mixture gives on reduction a titration curve with one single inflection corresponding to the sum of the values of the U^{+4} solution equivalent to each constituent. Thus the experimental end-point of 17.45 ml 0.073N U^{+4} is $= 3.30 + 7.30 + 6.85$ ml 0.073N U^{+4} corresponding to 5 ml 0.0481N Ce^{+4} , 5 ml 0.1066N $KMnO_4$ and 5 ml 0.10N $K_2Cr_2O_7$.

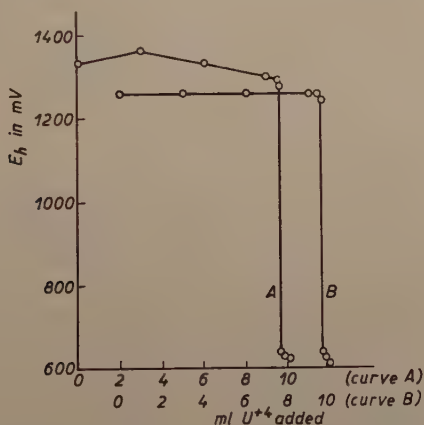


Fig. 5. Titration of 10 ml 0.100N $KBrO_3$ with 0.1030N U^{+4}
(A) in 3.3N H_2SO_4
(B) in 3.3N HCl

V. Reduction of bromate

In predicting the reducibility of bromate with U^{+4} , use was made of the redox potential of the system BrO_3^-/Br^- as calculated from free energy data amounting to 1.44 V³. The formal values as computed from the titration curves (Fig. 5) amount to 1.34-1.39 V in 2-6N H_2SO_4 , 1.22-1.26 V in 2-4N HCl and 1.39 V in 4N HNO_3 . These formal potentials together with the E_0 value of the BrO_3^-/Br^- system permit at the various acidities studied complete reduction of BrO_3^- with U^{+4} . The degrees of completion as calculated from these data and the potentials of U^{+6}/U^{+4} system amount to $2.3 \cdot 10^{-9}$ in 2N HCl and $3.9 \cdot 10^{-10}$ in 2N H_2SO_4 . This is essentially confirmed by the results shown in Table V. The titration curves are smooth and characterized by sharp inflections at the end-points which are more pronounced at lower than higher acidities and in presence of H_2SO_4 and HCl than HNO_3 .

As to the speed of the reaction under these conditions it was found that it takes place rapidly at the beginning of the titration but slows considerably at the end-point, needing 60 min. It could however be accelerated by adding few drops of a dilute ferric chloride solution, when only 15 minutes were found sufficient for the attainment of equilibrium. However, owing to the rapidity of the reaction at the beginning of the titration and the tendency of the potential to drift only at the end-point it is possible to trace the end of the reaction without awaiting the attainment of equilibrium.

TABLE V

Acidity	Max. inflection per 0.1 ml U^{+4} mV	Theoretical end-point ml	Exptl. end-point ml	Error %
Titration of 10 ml 0.0999N $KBrO_3$ with 0.103N U^{+4}				
5N HNO_3	249	9.70	9.67	-0.31
3.3N H_2SO_4	644	9.70	9.66	-0.41
8N "	249	9.70	9.66	-0.41
3.3N HCl	639	9.70	9.68	-0.21
6N " *	426	14.56	14.52	-0.27

* 15 ml BrO_3^- used.

VI. Titration of telluric acid

The redox potential of the Te^{+6}/Te^{+4} couple in acid solutions amounting to 1.02 volt³ permits the reduction of Te^{+6} to Te^{+4} . However, as may be seen from the titration curves, the formal potential values amount to 0.550 volt which is not appreciably different from the E_f values of the U^{+6}/U^{+4} system at 1N acid. However, the titration could be successfully performed only at room temperature in presence of 0.1-4.5N H_2SO_4 or 0.1-0.5N HCl , since reactions performed at 60° C are associated with considerable errors. Under all conditions shown in Table VI the reaction takes from 5-10 min for the attainment of equilibrium.

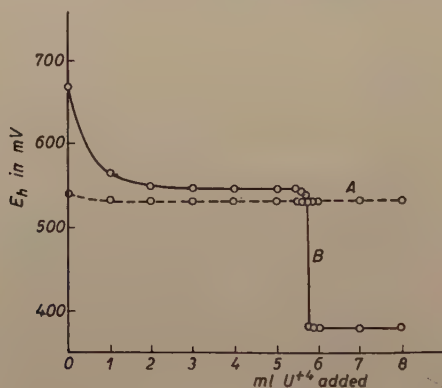


Fig. 6. Titration of 5 ml 0.07026N telluric acid with 0.0611N U^{+4}
(A) in 1N HCl
(B) in 0.1N H_2SO_4

TABLE VI

Acidity	Max. inflection per 0.1 ml U ⁺⁴ mV	Equilibrium time	Theoretical end-point ml	Exptl. end-point ml	Error %
Titration of 5.0 ml 0.07026 <i>N</i> telluric acid with 0.0611 <i>N</i> U ⁺⁴ at 25° C					
aqueous	66	20 min	5.75	5.75	nil
0.1 <i>N</i> H ₂ SO ₄	57	10 "	5.75	5.77	+0.35
4.5 <i>N</i> "	19	5 "	5.75	5.74	-0.17
6 <i>N</i> "	No inflection				
0.1 <i>N</i> HCl	27	5 "	5.75	5.75	nil
0.5 <i>N</i> "	42	10 "	5.75	5.75	"
1 <i>N</i> "	No inflection				
Titration of 5.0 ml 0.07026 <i>N</i> telluric acid with 0.0911 <i>N</i> U ⁺⁴ at 60° C					
1 <i>N</i> H ₂ SO ₄	131	1 min	3.86	3.15	-18.39
6 <i>N</i> "	25	10 "	3.86	4.05	+ 4.92

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The authors wish to express their thanks to Prof. Dr. A. RIAD TOURKY for his interest and criticism.

SUMMARY

Quadrivalent uranium can further be used for the estimation of $K_2Cr_2O_7$, $KMnO_4$ (in acid or alkali), H_2TeO_4 and $KBrO_3$ either alone or in conjunction with Fe^{+3} , Ce^{+4} and V^{+5} . The reaction proceeds rapidly in dilute acid solutions and especially when Fe^{+3} iron is used as a catalyst. Reduction of aqueous $KMnO_4$ gives MnO_2 which then dissolves in the acid of the reagent and undergoes reduction to Mn^{+2} . In acid solutions no MnO_2 separates. In alkaline medium (1.5-3N NaOH) $KMnO_4$ is reduced absolutely to MnO_2 .

RÉSUMÉ

L'uranium(IV) peut être utilisé pour le dosage de $K_2Cr_2O_7$, $KMnO_4$, H_2TeO_4 et $KBrO_3$, soit seuls, soit en présence de fer(III), de cérium(IV) et de vanadium(V). Ces réactions de réduction sont rapides, en solutions acides diluées, et surtout en présence de fer(III) comme catalyseur. La réduction de la solution aqueuse de $KMnO_4$ donne MnO_2 ; ce dernier se dissout ensuite dans l'acide et se réduit en Mn^{+2} . En solutions acides, on ne voit pas la formation de MnO_2 , tandis qu'en milieu alcalin (NaOH, 1.5 à 3N), $KMnO_4$ se réduit quantitativement en MnO_2 .

ZUSAMMENFASSUNG

Uran(IV) kann für die Bestimmung von $K_2Cr_2O_7$, $KMnO_4$, H_2TeO_4 und $KBrO_3$ allein oder in Gegenwart von Eisen(III), Cer(IV) oder Vanadin(V) angewendet werden. Diese Reduktionsreaktionen verlaufen in verdünnten Säurelösungen und vor allem bei Gegenwart von Eisen(III) als Katalysator schnell. Die Reduktion der wässrigen $KMnO_4$ -Lösung ergibt MnO_2 ; letzteres löst sich nachher in der Säure und reduziert sich zu Mn^{+2} . In sauren Lösungen scheidet sich kein MnO_2 aus, während $KMnO_4$ in alkalischem Milieu (1.5 bis 3N NaOH) quantitativ zu MnO_2 reduziert wird.

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POLAROGRAPHIC HALF-WAVE POTENTIALS OF METAL IONS IN VARIOUS SUPPORTING ELECTROLYTES. I

by

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INTRODUCTION

In recent years it has become increasingly apparent that many polarographic investigations would be greatly facilitated by the availability of systematic data on the half-wave potentials, wave forms, reversibilities, *etc.*, of a large number of metal ions in various supporting electrolytes. The uses to which such data can be put, and the recent investigations in which they have been collected, have been summarized in an accompanying paper¹. In this paper there are presented data concerning the polarographic characteristics of 28 metal ions in 9 supporting electrolytes. Two of these (1*M* potassium thiocyanate and 0.1*M* pyridine-pyridinium chloride) have been studied, though less comprehensively, by various authors whose results have been tabulated elsewhere⁴.

EXPERIMENTAL

All polarograms were recorded with a calibrated pen-and-ink recording polarograph³. A modified H-cell equipped with a sintered-Pyrex gas-dispersion cylinder to permit rapid deaeration⁵ was used. Such cells are now available from E. H. Sargent and Co. (S-29438). The dropping mercury electrode assembly was entirely conventional.

Solutions were prepared from reagent grade chemicals, and were always 1 millimolar in the metal ion being studied, except for those containing thallium(I), which were always 0.2 millimolar. The alkaline pyrophosphate solution was freshly prepared every day or two to avoid ambiguities which might have resulted from extensive hydrolysis of the pyrophosphate. No maximum suppressor was used except where specifically noted.

The reliability of the data was ensured by frequent measurement of the half-wave potential of cadmium(II) in 0.1*M* potassium chloride. Whenever the measured value deviated by more than 2-3 millivolts from the accepted value, -0.578 volt *versus* S.C.E., the saturated calomel electrode and saturated potassium chloride -4% agar bridge were replaced.

The measured half-wave potentials have been corrected both for the *iR* drop in the cell circuit and for the errors in the polarograph voltmeters.

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DATA AND DISCUSSION

The data secured are presented in Tables I-IX. Attention is directed to the following symbols: ">o" indicate that the wave merges with the anodic wave due to the dissolution of mercury or, in the ammoniacal and alkaline hydrazine media, with the anodic wave due to oxidation of the hydrazine. "NR" indicates that no wave, either cathodic or anodic, is observed. "W.-d." and "i.-d." mean well- and ill-defined, respectively, and refer to the precision which, in our opinion, could be achieved in the measurement of the wave height. Thus, a "very w.-d." wave could be used as the basis of a very precise analytical method, whereas a "very i.-d." wave would be useless for analytical purposes, and in fact would probably render impossible the precise measurement of the diffusion current of a wave which followed it.

(Contribution No. 1325 from the Department of Chemistry of Yale University).

TABLE I

HALF-WAVE POTENTIALS IN 1M POTASSIUM THIOCYANATE

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Ag(I)	>o -0.59 -1.14	o	Small acute max., w.-d. Very w.-d., $i = 1/4 i_1$ Very irreversible, probably anomalous
Ag(I) ^a	>o -1.43 -1.63	o	Max. increased in height, very w.-d. Probably anomalous
As(III) ^b	-0.68 -1.09 -1.56		Fairly w.-d., irreversible I.-d., irreversible Very i.-d.
As(III) ^{a,b}	-0.70 -1.13 -1.61	o(film?) -III(?) ?	W.-d., height halved by Triton Fairly w.-d., very irreversible I.-d., total wave height unchanged by Triton
As(V)	NR		
Bi(III)	>o -0.56	o	Fairly w.-d. Small, w.-d.
Bi(III) ^b	>o	o	Very w.-d.
Cd(II)	-0.651 -1.27	o	Very small rounded max., fairly w.-d., reversible Anomalous
Ce(IV)	-0.526	III(?)	Very w.-d., slightly irreversible
Co(II)	-1.084	o	Fairly i.-d., slightly irreversible
Cr(III)	-1.05	II	Fairly w.-d., very irreversible. May actually be poorly resolved double wave.
Cr(VI)	>o -0.46 -0.94	? ? II	Small, w.-d. Very small, w.-d. Main wave: fairly i.-d., irreversible
Cu(II)	>o -0.537	? o	About one-fourth of total wave height; w.-d., diffusion-controlled Acute max., fairly w.-d., slightly irreversible
Cu(II) ^a	>o -0.535	? o	<i>Vide supra</i> Very w.-d., slightly irreversible. Total wave height decreased ca. 10% by Triton

TABLE I (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Fe(II) ^c	-1.52	0	I.-d.
Fe(III) ^c	>0	II	Fairly w.-d.; very w.-d. with 0.002% Triton X-100
H(I)	-1.55 ₈	0	W.-d., irreversible
In(III)	-0.717	?	Fairly w.-d. (plateau has appreciable negative slope), large rounded min. at -1.4 V, $E_{3/4} - E_{1/4} = -22$ mV.
	-1.73	?	Fairly w.-d., height approx. equal to that of first wave, $E_{3/4} - E_{1/4} = -63$ mV.
Mn(II)	-1.540	0	Fairly w.-d., nearly reversible
Mo(VI)	NR		
Ni(II)	-0.685	0	Fairly w.-d.; rounded max. at -1.0 V; nearly reversible
Pb(II)	-0.435	0	W.-d., reversible
	-1.33		Anomalous
Pb(II) ^a	-0.445	0	Very w.-d., reversible
Sb(III) ^a	>0	0	Very w.-d.
Sb(V)	NR		
Sn(II)	-0.46	0	Huge rounded max., very i.-d. Precipitation occurs on standing.
Sn(IV) ^d	-0.50	0(?)	Large rounded min. at -1.1 V, very i.-d.; practically unchanged by 0.002% Triton X-100
Te(VI)	-1.1	?	Small very i.-d. pre-wave
	-1.4	?	Fairly w.-d., irreversible
Te(VI) ^a	-1.10	?	Very small, fairly i.-d.
	-1.46	?	W.-d., irreversible
Tl(I)	-0.522	0	Fairly w.-d., reversible
	-1.07		Probably anomalous
U(VI)	-0.24	V	I.-d., reversible (?)
	-0.54	IV + V	W.-d.
	-1.21	IV	W.-d., very irreversible
U(VI) ^a	-0.26 ₀	V	Very w.-d., reversible
	-1.32	IV	Fairly w.-d., irreversible
V(IV) ^e	-1.11	II	Fairly i.-d., very irreversible
V(V) ^e	-0.62	IV	Fairly w.-d.
	-1.26	II	Fairly i.-d.
W(VI) ^a	NR		
Zn(II)	-1.05 ₅	0	Fairly w.-d., reversible, includes anomalous wave
Zn(II) ^a	-1.05 ₈	0	W.-d., reversible
	-1.55		Anomalous

a: With 0.002% Triton X-100

d: 0.02M hydrochloric acid present

b: 0.001M hydrochloric acid present

e: 1M ammonium acetate present

c: 0.002N sulfuric acid present

TABLE II

HALF-WAVE POTENTIALS IN 10M POTASSIUM THIOCYANATE

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Ag(I)	>0	0	Small acute max., fairly w.-d.
As(III) ^a	-0.69	0(film?)	Small, w.-d., irreversible
	-1.50	-III(?)	Very w.-d., nearly reversible

TABLE II (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
As(V)	NR		
Bi(III)	>0	0	Fairly w.-d.; very w.-d. with 0.002% Triton X-100
Cd(II)	-0.778 -1.73	0	W.-d., reversible Probably anomalous
Ce(IV)	>0	III	Very w.-d.
Co(II)	-1.127	0	Very w.-d., irreversible
Cr(III)	-0.86 ₀ -1.35 ₈	II 0(?)	Fairly w.-d., irreversible I.-d., very irreversible
Cr(VI)	>0 -0.6 -0.96 ₃	? ? ?	Very i.-d. Very w.-d. Fairly i.-d., irreversible
Cu(II)	>0 -0.76 -1.21	I(?) 0(?)	Fairly w.-d. Fairly i.-d., reversible (?)
Cu(II) ^b	>0 -0.77 -1.28	I(?) 0(?)	W.-d. Fairly w.-d., reversible (?)
Fe(II) ^c	-1.41	0	Possibly anomalous Fairly w.-d., irreversible, preceded by hydrogen wave
Fe(III) ^c	>0 -1.43	II 0	Very w.-d. W.-d., very irreversible
H(I)	-1.13 ₂	0	W.-d., very irreversible
In(III)	-0.68 ₇	?	Fairly i.-d.: small min. at -1.0 V followed by very large min. at -1.5 V, $E_{3/4}-E_{1/4} = -29$ mV
Mn(II)	-1.63 ₀	0	I.-d., slightly irreversible
Mo(VI)	-1.51 ₇	?	Abnormally small, i.-d., irreversible
Ni(II)	-0.764	0	W.-d. except for large rounded max. at -1.2 V, nearly reversible
Pb(II)	-0.575	0	Small acute max., fairly i.-d., reversible
Pb(II) ^b	-0.575	0	Very w.-d., reversible
Sb(III)	>0	0	W.-d.
Sb(V)	NR		
Sn(II)	-0.56	0	Small max., i.-d., reversible
Sn(IV) ^d	-0.60	0(?)	Small, fairly w.-d., irreversible
Te(VI)	-1.04 -1.23 -1.39	? ? ?	Very small, fairly w.-d. Small, very i.-d. W.-d., irreversible
Tl(I)	-0.678 -1.25	0 0	W.-d., reversible Anomalous
Tl(I) ^b	-0.679 -1.39	0	W.-d., reversible Anomalous
U(VI)	>0	V(?)	Fairly i.-d., rounded max. at -1.05 V
V(IV) ^e	-1.00 ₄	II	W.-d., very irreversible
V(V) ^e	-0.71 -1.02	IV II }	Two very i.-d. irreversible waves
W(VI)	NR		
Zn(II)	-1.18 ₇	0	Very w.-d., reversible

a: 0.001M hydrochloric acid present

b: With 0.002% Triton X-100

c: 0.002M sulfuric acid present

d: 0.02M hydrochloric acid present

e: 1M ammonium acetate present

TABLE III

HALF-WAVE POTENTIALS IN SATURATED HYDRAZINE DIHYDROCHLORIDE

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Ag(I)	>0	0	Very w.-d.
As(III)	-0.192	0(film?)	W.-d., irreversible
	-0.575		Fairly w.-d., abnormally steep
As(V)	NR		
Bi(III)	-0.197	0	Very w.-d., reversible
Cd(II)	-0.729	0	Fairly w.-d., reversible
Ce(III)	NR		
Ce(IV)	-		Rapidly reduced to Ce(III), <i>q.v.</i>
Co(II)	NR		
Cr(III)	NR		
Cr(VI)	-0.590	III(?)	Fairly i.-d., irreversible
Cu(II)	>0	I	Very w.-d.
	-0.326	0	Very w.-d., reversible
Fe(II)	NR		
Fe(III)	>0	II	Very w.-d.
In(III)	-0.648	I(?)	W.-d., $E_{1/2} - E_{1/4} = -25$ mV
	-0.90 ₈	0(?)	Fairly w.-d., $E_{1/2} - E_{1/4} = -53$ mV, height = 1/3 that of total double wave
Mn(II)	NR		
Mo(V)	>0	IV	W.-d.
	-0.435	III	W.-d., irreversible
Mo(VI)	-		Rapidly reduced to Mo(V), <i>q.v.</i>
Ni(II)	NR		
Pb(II)	-0.544	0	Very w.-d., reversible
Sb(III)	-0.197	0	Very w.-d., nearly reversible
Sb(V)	>0	III	I.-d.
	-0.21	0	Very w.-d., irreversible
Sn(II)	-0.25		Small fairly w.-d. pre-wave
	-0.53 ₅	0	W.-d., reversible
Sn(IV)	-0.21	II	Very w.-d., irreversible
	-0.52 ₂	0	W.-d., reversible
Te(VI)	-0.747	?	Small w.-d. wave; final current rise begins abnormally early but no second plateau is observed
Tl(I)	-0.562	0	Very w.-d., reversible
U(VI)	-0.15 ₈	IV	Very w.-d.
	-0.88 ₅	III	W.-d.
V(IV)	-0.94	II	Large acute max., very i.-d., irreversible
V(IV) ^a	-0.99	II	Max. somewhat reduced, i.-d., irreversible
V(V)	-0.5	?	Small i.-d. pre-wave
	-0.9		Very i.-d., very irreversible
W(VI)	NR		Extensive pptn. of WO ₃ from a 1 mM soln.
Zn(II)	-0.98 ₃	0	I.-d., reversible

^a: With 0.002% Triton X-100

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TABLE IV

HALF-WAVE POTENTIALS IN 1*M* HYDRAZINE — 1*M* AMMONIA — 1*M* AMMONIUM CHLORIDE

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Ag(I) ^a	>0	o	Very w.-d.; i_d decreases on standing as Ag(I) is reduced by N ₂ H ₄
As(III)	-1.11 -1.35 ₆	o(film(?)) o(?)	Small pre-wave Small max., fairly w.-d., irreversible. Final current rise (actually max. of next wave) begins about -1.5 V
As(III) ^a	-1.11 -1.30	o(film(?)) o(?)	Small pre-wave Large max., fairly w.-d., irreversible
	-1.56 ₅		Large max., irreversible
As(V)	NR		
Bi(III) ^b	-1.60	o	Very i.-d., irreversible
Bi(III) ^{a,b}	-1.54	o	I.-d., irreversible
Cd(II)	-0.82 ₃	o	Fairly i.-d., reversible
Cd(II) ^a	-0.84 ₂ -1.56	o	Very w.-d., irreversible I.-d., anomalous
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), <i>q.v.</i>
Co(II)	-1.29	o	Plateau very irregular, with series of alternating maxima and minima
Co(II) ^a	-1.28 ₅ -1.45	o	Fairly w.-d., slightly irreversible Fairly w.-d., probably anomalous
Cr(III)	-1.40 ₂ -1.7	II o	W.-d., reversible Very i.-d. Soln. pink, slightly turbid
Cr(VI→III)	-1.40 ₀ -1.7	II o	Very w.-d., reversible Very i.-d. Soln. pink, no visible ppt.
Cu(I)	-0.52 ₁	o	Fairly w.-d., reversible
Cu(II)	—		Rapidly reduced to Cu(I), <i>q.v.</i>
Fe(II)	-1.49 ₂	o	Large acute max., fairly w.-d.
Fe(II) ^a	-1.47 ₃	o	Fairly w.-d., slightly irreversible. No visible ppt.
Fe(III) ^b	-1.09 ₁ -1.48 ₅	II o	W.-d., irreversible W.-d., slightly irreversible. $i_2/i_1 = 4$; probably partial reduction of Fe(III) by N ₂ H ₄
In(III) ^b	-0.90 ₁	?	Fairly w.-d., irreversible
Mn(II)	-1.11 ₆	o	Acute max., fairly i.-d., probably slightly irreversible.
Mn(II) ^a	-1.11 ₆	o	Max. unchanged, fairly i.-d.
Mo(VI)	-1.71 ₈	V(?)	I.-d., $E_{3/4}-E_{1/4} = 45$ mV
Ni(II)	-1.07 ₉	o	Large rounded max., fairly w.-d., reversible (?)
Ni(II) ^a	-1.06 -1.14	 o	Very i.-d., height approx. 1/3 that of total double wave Very w.-d., irreversible, acute max. at -1.65 V
Pb(II)	-0.42 -0.51 ₂	 o	Small irreversible pre-wave Fairly i.-d., reversible
Sb(III)	-0.74 ₂ -1.6	o ?	Fairly w.-d., irreversible Very i.-d.
Sb(V)	NR		
Sn(II) ^b	(-0.634) -0.77 ₃ -1.62	IV o	W.-d., irreversible W.-d., reversible I.-d., anomalous (?)

TABLE IV (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Sn(II) ^{a,b}	(-0.640) -0.779 -1.62	IV o	Very w.-d., irreversible W.-d., reversible I.-d., anomalous (?)
Sn(IV)	-1.13 -1.35	II o	Very i.-d., irreversible Very i.-d., irreversible
Sn(IV) ^a	-1.26 -1.57	II o	I.-d., irreversible I.-d., irreversible
Te(IV)	-0.714		Very w.-d. with characteristic large acute max. at -1.2 V., $E_{1/2}-E_{1/4} = -57$ mV
Te(VI)	—		Rapidly reduced to Te(IV), <i>q.v.</i>
Tl(I)	-0.487	o	Fairly w.-d., reversible
U(VI) ^b	NR		
V(IV)	-1.20 ₉ -1.49	III(?) II(?)	Fairly w.-d., irreversible I.-d., irreversible. Soln. becomes turbid yellow on standing; waves are abnormally small
V(V)	-1.146	?	Very w.-d., irreversible
W(VI)	NR		
Zn(II)	-1.330	o	Small acute max., fairly w.-d., reversible, includes contribution from anomalous wave
Zn(II) ^a	-1.330 -1.58	o	W.-d., reversible I.-d., anomalous

TABLE V

HALF-WAVE POTENTIALS IN 1*M* HYDRAZINE — 1*M* SODIUM HYDROXIDE

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Ag(I) ^a	NR		
As(III)	NR		
As(V)	NR		
Bi(III)	-0.70	o	Very i.-d., slightly irreversible large rounded max. at -1.4 V
Bi(III) ^b	-0.705 -1.54	o	Very w.-d., slightly irreversible I.-d., irreversible, possibly anomalous
Cd(II) ^a	-0.70 ₁ -0.81 ₃	o o	Very i.-d., nearly reversible W.-d., reversible
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), <i>q.v.</i>
Co(II) ^a	-1.42 ₃	o	W.-d., nearly reversible
Cr(III)	NR		
Cr(VI)	-0.93	III	Fairly w.-d., very irreversible
Cu(II) ^a	-0.8	?	Very small, i.-d.
Fe(II)	(-0.59) -1.38	III o	Fairly w.-d., irreversible I.-d., irreversible
Fe(III) ^a	-0.97 -1.58	II o	I.-d., irreversible Fairly w.-d., slightly irreversible
In(III)	-1.15 -1.30	? ?	I.-d., $E_{1/2}-E_{1/4} = -31$ mV Very i.-d., very irreversible, height = approx. 2/3 that of total double wave

TABLE V (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
In(III) ^b	-1.20 -1.54	? ?	Fairly w.-d., irreversible I.-d., irreversible, height = approx. $1/2$ that of total double wave
Mn(II)	NR		
Mo(VI)	NR		
Ni(II)	NR		
Pb(II)	-0.76 ₉	o	Fairly i.-d., irreversible, includes contribution from anomalous wave
Pb(II) ^b	-0.769 -1.58	o	Very w.-d., reversible Anomalous
Sb(III)	-1.20 ₇	o	W.-d., irreversible
Sb(V)	NR		
Sn(II)	(-0.873) -1.219	IV o	Small max., fairly w.-d., slightly irreversible Fairly w.-d., irreversible, includes contribution from anomalous wave
Sn(II) ^b	(-0.851) -1.219 -1.57 ₂	IV o	Very w.-d., slightly irreversible Very w.-d., irreversible Anomalous
Sn(IV)	NR		
Te(VI)	-1.4	?	I.-d., irreversible
Te(VI) ^b	-1.21	?	Fairly w.-d.; $E_{3/4}-E_{1/4} = -29$ mV
Tl(I)	>0	o	Fairly i.-d.
U(VI)	-0.98 ₀	?	W.-d., irreversible
V(IV)	NR		
V(V)	NR		
W(VI)	NR		
Zn(II)	-1.52 ₅	o	Rounded max., fairly w.-d., slightly irreversible

a: Extensive precipitation from a 1 mM solution

b: With 0.002% Triton X-100

TABLE VI

HALF-WAVE POTENTIALS IN 10M SODIUM HYDROXIDE

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Ag(I) ^a	>0	o	
As(III)	(-0.337)	V	Fairly w.-d., slightly irreversible
As(V)	NR		
Bi(III)	-0.74 ₃	o	Acute max., w.-d., slightly irreversible
Bi(III) ^b	-0.67 ₀	o	Very w.-d., nearly reversible
Cd(II)	-0.91 ₃	o	Large rounded max., fairly i.-d., reversible
Ce(IV) ^a	NR		
Co(II)	-1.58 ₄	o	Fairly w.-d., slightly irreversible
Cr(III)	-1.08	II	Very i.-d., irreversible
Cr(VI)	-0.837	III	Very w.-d., irreversible
Cu(II)	-0.55 ₃	o	Small max., fairly w.-d., slightly irreversible
Cu(II) ^b	-0.54 ₇	o	Max. greatly reduced, very w.-d., slightly irreversible
Fe(II) ^a	(-1.05 ₀) -1.67 ₃	III o	Fairly w.-d., reversible Fairly i.-d.

TABLE VI (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Fe(III) ^a	-1.055	II	W.-d., reversible
In(III)	-1.38 ₂	?	Fairly w.-d., irreversible
Mn(II) ^a	(-0.477)	III(?)	Very w.-d., irreversible
Mo(VI)	NR		
Ni(II)	NR		
Pb(II)	-0.83 ₂	o	Acute max., w.-d., reversible
Pb(II) ^b	-0.82 ₅	o	Very w.-d., reversible
Sb(III)	(-0.573)	V	W.-d., slightly irreversible
	-1.246	o	Very w.-d., irreversible
Sb(V)	NR		
Sn(II)	(-1.14 ₄)	IV	Large max., w.-d., reversible
	-1.19 ₈	o	Large max., w.-d., reversible
Sn(IV)	NR		
Te(VI)	NR		
Tl(I)	-0.453	o	Fairly w.-d., reversible, rounded max. at -1.0 V
	-1.20		Probably anomalous
Tl(I) ^b	-0.458	o	Very w.-d., reversible
U(VI) ^a	-0.95 ₅	V(?)	W.-d., irreversible
V(IV)	(-0.558)	V	W.-d., slightly irreversible
V(V)	NR		
W(VI)	NR		
Zn(II)	-1.60 ₇	o	Fairly w.-d., slightly irreversible

a: Extensive precipitation from a 1 mM solution

b: With 0.002% Triton X-100

TABLE VII

HALF-WAVE POTENTIALS IN 0.1M PYRIDINE — 0.1M PYRIDINIUM CHLORIDE

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Ag(I)	>0	o	I.-d.
As(III)	-0.90		I.-d., irreversible
	-1.05		I.-d., irreversible
As(V)	NR		
Bi(III) ^a	-1.00	o	I.-d., irreversible
Bi(III) ^{a,b}	-0.81		Small irreversible pre-wave
	-1.15		I.-d., irreversible
Cd(II)	-0.617	o	Very w.-d., reversible
Ce(IV) ^a	NR		Apparently complete pptn.
Co(II)	-1.050	o	I.-d.
Co(II) ^b	-1.050	o	Very w.-d., reversible (?)
Cr(III)	-0.986	II	Fairly i.-d., irreversible
Cr(VI)	>0	III	Large max., w.-d.
	-1.19	II	Fairly w.-d.
Cr(VI) ^b	>0	III	Max. incompletely suppressed, w.-d.
	-1.20	II	Fairly w.-d.
Cu(II)	>0	I	W.-d.
	-0.229	o	Large rounded max., fairly w.-d.
Cu(II) ^b	>0	I	W.-d.
	-0.219	o	Max. incompletely suppressed, w.-d.
Fe(II)	NR		
Fe(III) ^a	NR		Apparently complete pptn.
In(III)	NR		No visible pptn.

TABLE VII (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Mn(II)	NR		
Mo(VI)	-0.237		Fairly w.-d. very small pre-wave
	-0.680	?	W.-d., irreversible
Ni(II)	-0.742		Acute max., fairly w.-d., reversible (?)
	-1.15 ₉		Irreversible, $i = 1/7 i_1$
Ni(II) ^b	-0.751		Very w.-d., reversible (?)
	-1.16 ₅		W.-d., irreversible, $i = 1/7 i_1$
Pb(II)	-0.398	o	W.-d., reversible
Sb(III)	-0.47 ₂		I.-d., irreversible
Sb(III) ^b	-0.574		I.-d., irreversible
	-0.75 ₂		Very w.-d., irreversible, $i = 2/3 i_1$, total height unchanged by Triton
Sb(V)	NR		
Sn(II) ^a	-1.12	o	Fairly w.-d., irreversible
Sn(IV)	NR		
Te(VI)	NR		
Tl(I)	-0.451	o	Very w.-d., reversible
U(VI)	-0.22 ₈	V(?)	Fairly w.-d.
	-0.45 ₀	IV(?)	W.-d.
	-0.97 ₈	III(?)	Fairly w.-d., irreversible
V(IV)	-0.63	?	Very i.-d., irreversible
V(IV) ^b	-0.87 ₄	?	Fairly w.-d., irreversible
V(V)	-0.10 ₇	IV	Fairly w.-d., irreversible
	-0.43 ₁		W.-d., irreversible, $i = 1/2 i_1$
	-0.77 ₂	II	W.-d., irreversible, $i = 3/2 i_1$
W(VI)	NR		
Zn(II)	-1.032	o	Fairly w.-d., reversible

a: Extensive pptn. from a 1 mM solution

b: With 0.002% Triton X-100

TABLE VIII

HALF-WAVE POTENTIALS IN 1M PYRIDINE — 1M SODIUM HYDROXIDE

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Ag(I) ^a	>0	o	Very i.-d.
As(III)	(-0.235)	V	Fairly w.-d., reversible
As(V)	NR		
Bi(III) ^a	-1.17 ₉	o	I.-d., irreversible
Cd(II) ^a	NR		Apparently complete pptn.
Ce(IV) ^a	NR		Large white ppt.
Co(II) ^a	-1.61	o	Fairly i.-d., irreversible, blue turbidity
Cr(III)	NR		
Cr(VI)	-1.46 ₇	III(?)	I.-d., very irreversible
Cr(VI) ^b	-1.47 ₆	III(?)	Fairly w.-d., very irreversible
Cu(II) ^a	-0.30 ₆		Small irreversible pre-wave
	-1.06		Max., very i.-d., irreversible
Cu(II) ^{a,b}	-0.93		I.-d., irreversible
Fe(II)	NR		
Fe(III) ^a	-0.56	II	W.-d., very irreversible
	-1.53	o	Fairly i.-d., irreversible
In(III)	NR		No visible pptn.
Mn(II)	-1.53		Small irreversible pre-wave
	-1.72	o	I.-d.

TABLE VIII continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Mo(VI)	NR		
Ni(II)	NR		No visible pptn.
Pb(II)	-0.83		Small pre-wave
	-1.15		Fairly i.-d., irreversible
Pb(II) ^b	-1.15		I.-d., irreversible
Sb(III)	(-0.232)	V	W.-d., reversible
Sb(V)	NR		
Sn(II)	(-0.483)	IV	Very w.-d., slightly irreversible
	-1.54		Small irreversible pre-wave
	-1.71	o	W.-d., abnormally high, probably includes contribution from anomalous wave
Sn(IV)	NR		
Te(VI)	NR		
Tl(I)	-0.48 ₉	o	Fairly i.-d., irreversible
U(VI)	-1.56		I.-d.
V(IV)	NR		
V(V)	NR		
W(VI)	NR		
Zn(II)	-1.724	o	Fairly w.-d., abnormally steep ($E_{3/4}-E_{1/4} = ca. 3 \text{ mV}$)

a: Extensive precipitation from a 1 mM solution

b: With 0.002% Triton X-100

TABLE IX

HALF-WAVE POTENTIALS IN 1M SODIUM HYDROXIDE — SATURATED SODIUM PYROPHOSPHATE

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Ag(I) ^a	>0	o	Fairly w.-d.
	-0.97		Probably anomalous
As(III) ^a	NR		
As(V)	NR		
Bi(III) ^a	-0.68 ₁	o(?)	Fairly i.-d., irreversible
	-1.23	?	W.-d., irreversible, $i = 1/3 i_1$
Bi(III) ^{a,b}	-0.68 ₈	o(?)	Very w.-d., slightly irreversible
	-1.46	?	I.-d., irreversible, $i = 1/5 i_1$
	-1.67	?	Irreversible, $i = 1/2 i_1$
Cd(II) ^a	-0.79 ₃	o	Fairly w.-d., reversible
Cd(II) ^{a,b}	-0.78 ₃	o	Fairly w.-d., slightly irreversible
	-1.58	?	I.-d., possibly anomalous, $i = 3 i_1$
Ce(IV) ^a	NR		
Co(II) ^a	-1.45 ₄		Fairly w.-d., irreversible
	-1.82		I.-d., abnormally steep, $i = 1/5 i_1$
			Possibly two complexes in sluggish equilibrium
Co(II) ^{a,b}	-1.44 ₅		I.-d., irreversible, height decreased about 40% by Triton
	-1.60 ₄		W.-d., irreversible, $i = 4/5 i_1$
	-1.79		I.-d., abnormally steep, $i = 1/10 i_1$
Cr(III) ^{a(?)}	NR		
Cr(VI)	-0.82 ₁	III	I.-d., irreversible
	-1.04		W.-d., irreversible, possibly anomalous

TABLE IX (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
Cr(VI) ^b	-0.85 ₃	III	Very w.-d., irreversible, height decreased about 25% by Triton
	-1.44		} Fairly w.-d., irreversible, possibly anomalous
	-1.65		
Cu(II)	-0.35 ₇	o(?)	I.-d., reversible
	-0.44 ₀	o(?)	Small max.,
	-1.09		W.-d., probably anomalous
Cu(II) ^b	-0.35 ₅	o(?)	I.-d., reversible
	-0.44 ₀	o(?)	Very w.-d., nearly reversible
	-1.39		} Small, i.-d., probably anomalous
	-1.65		
Fe(II)	NR		
Fe(III) ^a	-0.96 ₈	II	Fairly w.-d., irreversible
	-1.55 ₉	o	Fairly w.-d., nearly reversible, $i < 2 i_1$
Fe(III) ^{a,b}	-0.93 ₆	II	Very w.-d., irreversible
	-1.54 ₆	o	I.-d., slightly irreversible, $i > 2 i_1$
In(III) ^a	-1.12		I.-d., irreversible
	-1.28		Fairly w.-d., irreversible, $i = 3/4 i_1$
In(III) ^{a,b}	-1.13 ₀	?	W.-d., $E_{1/2} - E_{1/4} = -57$ mV
	-1.58 ₈	?	W.-d., irreversible, $i = 2 i_1$
Mn(II) ^a	-0.77		I.-d.
	-0.96		Two irreversible pre-waves of equal height, possibly due to Mn(III) formed (?)
	-1.71 ₁	o	Fairly w.-d., reversible
Mo(VI)	NR		
Ni(II) ^a	NR		
Pb(II)	-0.76 ₃	o	Fairly w.-d., reversible
	-1.14		Very i.-d., probably anomalous, $i = i_1$
Pb(II) ^b	-0.75 ₈	o	Very w.-d., reversible, height decreased about 20% by Triton
	-1.55		I.-d., probably anomalous, $i = 1/2 i_1$
Sb(III)	(-0.45 ₂)	V	Small max., w.-d., reversible
	-1.19 ₄	o	Fairly i.-d., irreversible, includes contribution from anomalous wave
Sb(III) ^b	(-0.43 ₉)	V	Very w.-d., slightly irreversible
	-1.19 ₄	o	Fairly i.-d., irreversible, contribution from anomalous wave reduced but not eliminated
Sb(V)	NR		
Sn(II)	(-0.89)	IV	Large max., w.-d.
	-1.16	o	Small max., fairly i.-d., includes contribution from anomalous wave
Sn(II) ^b	(-0.84)	IV	Very w.-d., irreversible
	-1.17	o	W.-d., irreversible
	-1.64		W.-d., anomalous
Sn(IV)	NR		
Te(VI)	-1.54 ₀		Large acute max., i.-d., irreversible
Te(VI) ^b	-1.56 ₁		Max. greatly reduced, i.-d., irreversible
Tl(I) ^a	-0.51 ₀	o	Fairly w.-d., reversible
	-1.21		I.-d., probably anomalous, $i = 2 i_1$
U(VI) ^a	-0.92 ₆	IV(?)	I.-d., $E_{1/2} - E_{1/4} = -63$ mV
	-1.12 ₃	III(?)	Fairly w.-d., irreversible, $i = 1/2 i_1$

TABLE IX (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E., volts	Oxidation state of product	Notes
V(IV)	(-0.438)	V	Very w.-d., reversible
V(V)	NR		
W(VI)	NR		
Zn(II)	-1.50 ₂	o	I.-d., irreversible
	-1.73 ₇		Fairly w.-d., irreversible, $i = 1/5 i_1$
Zn(II) ^b	-1.50 ₂	o	Very i.-d., irreversible
	-1.71 ₈		Fairly w.-d., irreversible, $i = 3/4 i_1$

a: Extensive precipitation from a 1 mM solution

b: With 0.002% Triton X-100

SUMMARY

Data on the polarographic half-wave potentials, wave characteristics, probable reduction products and other polarographically important information are tabulated for 28 metal ions in 9 supporting electrolytes containing hydrazine, pyridine, sodium hydroxide, potassium thiocyanate, and pyrophosphate.

RÉSUMÉ

Des tables de potentiels de demi-vagues polarographiques, de caractéristiques de sauts, de produits de réduction probables et d'autres renseignements polarographiques importants sont données pour 28 cations dans 9 électrolytes de base, renfermant de l'hydrazine, de la pyridine, de l'hydroxyde de sodium, du thiocyanate de potassium et du pyrophosphate.

ZUSAMMENFASSUNG

Es werden Tabellen gegeben mit polarographischen Halbwerts-Potentialen, Eigenschaften der Sprünge, wahrscheinlichen Reduktionsprodukten und mit anderen wichtigen polarographischen Auskünften für 28 Kationen in 9 Grund-Elektrolyten, welche Hydrazin, Pyridin, Natriumhydroxyd, Kaliumthiocyanat und Pyrophosphat enthalten.

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- ⁴ *ibid.*, Appendix B.
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BOOK REVIEW

Hefe und Alkohol sowie andere Gärungsprodukte, H. KRETZSCHMAR, Springer-Verlag, Berlin-Göttingen-Heidelberg 1955. XV + 648 pages, 176 illustrations, 3 diagrams. Price DM 66.—.

This thorough and comprehensive textbook on fermentation technology not only discusses the preparation of yeast, alcohol and yeast products, but also the preparation of other products using micro-organisms. In this connection mention can be made of the preparation of lactic acid, acetic acid, citric acid, acetone and a number of other compounds with special fermentation methods and the preparations of vitamins, dextran and antibiotics the development of which owes much to the experience of fermentation experts.

Analysts will be particularly interested in the section on analytical methods for molasses, yeast, alcohol etc., which comprise approximately one tenth of the book. The author in the rest of the book has described the many variations of the preparative methods but for the analytical section he has chosen to describe certain selected methods. Some of the methods are well-known, others are based on well-known principles, but the comprehensive description of the details of the methods shows a thorough investigation. However, the section on vitamin determinations is incomplete and cannot be substituted for the special books on this subject. The description of the tests which are so important for judging the quality of alcohol, namely, taste and smell is too brief. No mention is made of the technique of the tests or of the statistical evaluation of the results.

F. REIMERS (Copenhagen)

REVUES DE LIVRES

Chemical and Spectrographic Analysis of Magnesium and its Alloys, par A. MAYER et W. J. PRICE, Magnesium Elektron Ltd., Manchester, 1955, 248 p., 25 fig.; prix: 3 guineas.

Dans ce livre les auteurs ont rassemblé les méthodes d'analyse du magnésium et de ses alliages, recommandées par Magnesium Elektron Ltd. Ils n'ont pas la prétention de nous présenter „la meilleure méthode” pour le dosage de chaque élément, mais des méthodes qui, essayées pendant de longues périodes dans les laboratoires de Magnesium Elektron Ltd., ont donné des résultats très satisfaisants, et peuvent être considérées comme méthodes recommandables, directement applicables dans presque tous les cas qui peuvent se présenter.

La première partie est consacrée aux méthodes chimiques et physico-chimiques. Tous les éléments rencontrés à l'heure actuelle dans le magnésium et ses alliages y sont traités, par ordre alphabétique. La description des méthodes est remarquablement claire et complète. Une discussion élémentaire des principes théoriques qui sont à la base de chaque méthode décrite en permet l'application consciencieuse même pour des analystes ou des assistants non routinés.

La seconde partie du travail traite spécialement le dosage des différents éléments par analyse spectrographique. Après un aperçu des méthodes décrites dans la littérature, on y trouve un exposé bref des principes de la spectrographie, suivi de la description des méthodes employées par Magnesium Elektron Ltd. On pourrait regretter que la Firma n'ait pas encore appliqué jusqu'ici la méthode d'analyse directe, dont les données pratiques seraient très intéressantes.

La valeur du livre est augmentée du fait qu'il a été conçu dans le but de pouvoir le compléter, au fur et à mesure qu'elles apparaissent, par de nouvelles méthodes, plus exactes ou plus rapides, et par la description de méthodes d'analyse pour des éléments dont le dosage pourrait se justifier dans l'avenir.

Le livre est vivement recommandé à tous ceux qui sont intéressés à l'analyse du magnésium et de ses alliages.

J. EECKHOUT (Gand)

Polarographic Techniques, par L. MEITES, Interscience Publishers, Inc., New York, 1955, 317 pages, 44 fig., prix: \$ 6.00.

Le Professeur MEITES, bien connu pour ses travaux en polarographie, vient de faire paraître un ouvrage qui rendra de précieux services à tous ceux qui utilisent cette méthode.

On y trouve la description détaillée de la technique opératoire de la polarographie. L'auteur traite de l'appareillage et plus particulièrement des cellules, du capillaire et des électrodes de référence. Un chapitre est consacré à l'étude des courants résiduels, du courant de migration et des courants d'ordre catalytique. Un autre renferme la théorie de la courbe potentiel-courant. Plus loin, l'auteur examine la question du potentiel de demi-vagues et de son interprétation. Les chapitres suivants s'intitulent: maxima et leur élimination, technique de l'analyse polarographique quantitative, titration ampérométrique et techniques spéciales.

Cet ouvrage est fort bien présenté, la lecture en est aisée et l'exposé fort clair. A la fin de chaque chapitre, le lecteur trouvera, heureuse innovation, une série d'expériences pratiques minutieusement décrites et qui lui permettra d'acquérir une maîtrise parfaite de la technique polarographique.

A la fin du livre, l'auteur étudie les perturbations provenant du circuit polarographique. Il donne onze courbes potentiel-courant présentant des anomalies et dans chaque cas, il en donne l'origine et les moyens de les corriger.

Excellent ouvrage que nous recommandons vivement à tous ceux — et ils sont de plus en plus nombreux — qui utilisent cette élégante méthode.

D. MONNIER (Genève)

Traité de Micro-analyse Minérale, par CLÉMENT DUVAL, Presses Scientifiques Internationales, Paris, 1955, Tome II, 448 pages, 59 figures, prix: f. frs. 3000.

Respectant l'horaire qu'il s'était proposé, le Professeur CLÉMENT DUVAL vient de faire paraître le Tome II de son traité de micro-analyse minérale.

Nous ne pouvons que répéter ici ce que nous avons dit lors de la parution du Tome premier. La bibliographie est très importante et s'étend jusqu'à fin 1954, début 1955; chaque référence a été minutieusement choisie; une présentation impeccable malgré le prix modique de l'ouvrage; un texte clair et dépouillé.

Ce deuxième Tome a pour objet les groupes III A, IV A, V A, VI A et VII A. En outre, le lecteur trouvera des renseignements fort substantiels ainsi qu'une bibliographie succincte des éléments transuraniens.

Ce livre apporte aux chimistes une documentation de premier ordre; les méthodes classiques voisinent avec les procédés les plus modernes de l'analyse physico-chimique, avec la polarographie, colorimétrie, coulométrie, potentiométrie etc.

Nous sommes certains que le succès de cet ouvrage s'affirmera de plus en plus.

D. MONNIER (Genève)